



THE PENNSYLVANIA
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IONOSPHERIC RESEARCH

Scientific Report 387

THE PHOTOLYSIS OF OZONE

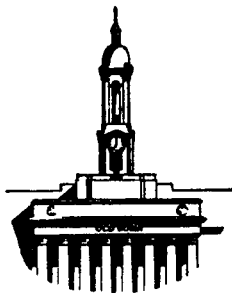
by

Eduardo Lissi and Julian Heicklen

February 4, 1972

The research reported in this document has been sponsored by the National Science Foundation under grant GA-12385 and in part by the National Aeronautics and Space Administration under grant NGL 39-009-003.

IONOSPHERE RESEARCH LABORATORY



University Park, Pennsylvania

(NASA-CR-130830) THE PHOTOLYSIS OF OZONE
(Pennsylvania State Univ.) 65 p HC
\$5.25

CSCI 04A

N73-18399

Unclass

G3/13 64237

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Scientific Report 387

"The Photolysis of Ozone"

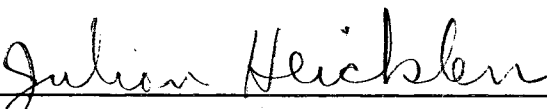
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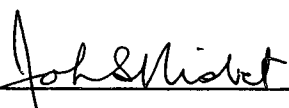
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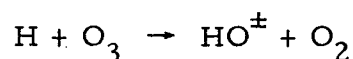
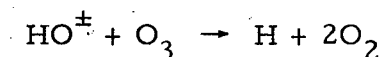
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ABSTRACT

Ozone was photolyzed at 25°C with steady illumination at several wavelengths from 2288-2850 Å, at O₃ pressures from 0.1 to 2.7 torr, and at absorbed intensities, I_a, from 0.15 to 65 μ/min. Experiments were done in pure dry O₃, and in the presence of He, CO₂, N₂, H₂O, H₂, N₂O, He-CO₂, He-H₂O, CO₂-H₂O, O₂-N₂O, CO₂-O₂ and N₂O₅-O₂-CO₂ mixtures.

The results show that in the absence of added gases or in the presence of He, the quantum yield of O₃ consumption, $-\Phi\{O_3\}$, is 5.5 independent of conditions, except at pressures below 0.4 torr, where the yield drops toward 5.0 because of wall deactivation. In the presence of CO₂ or N₂, $-\Phi\{O_3\}$ falls toward 4.0. The complete mechanism is outlined and it does not involve regeneration of O(¹D) in the chain step. The primary photolytic act produces O(¹D) and singlet O₂, presumably O₂(¹Δ), at all wavelengths below 3000 Å.

With H₂O present $-\Phi\{O_3\}$ increases in a chain reaction whose importance is proportional to [O₃] at constant [O₃]/[H₂O] ratios, varies inversely as I_a^{1/2}, and increases with [H₂O]^{1/2} at low H₂O vapor pressures, but becomes invariant or falls slightly with further increases in H₂O vapor pressure. The water chain is carried by the reactions



with HO[±] being vibrationally excited HO with $v \geq 2$. The chain is terminated by radical-radical processes at low H₂O vapor pressures, but deactivation

of HO^\pm by H_2O vapor can play a role at high H_2O vapor pressures. Some wall deactivation may also occur, but it is minor in our experiments.

In the presence of N_2O , $-\Phi\{\text{O}_3\}$ falls toward 4.0 at low conversions but reaches 2.8 at extended conversions. This decrease is not due to O_2 accumulation, but to N_2O_5 accumulation which removes either $\text{O}(^3\text{P})$ or $\text{O}_2(^1\Delta)$.

Relative quenching constants for $\text{O}(^1\text{D})$ removal by various gases were measured at 2288, 2537, and 2800 Å. In some cases the results are badly scattered, but they can be summarized as follows: For O_3 , CO_2 , and N_2 , the relative rates are 1.0/0.4-0.5/0.08-0.11 at all wavelengths. For H_2O the constant at 2537 Å is 1.5 relative to that for O_3 . With N_2O , a noticeable wavelength effect is observed and the relative rate constants are 1.5, 2-3, 4.0 for O_3 compared to N_2O at 2800, 2537, and 2288 Å, respectively. This variation must be due to the excess translational energy, which changes with wavelength, in the $\text{O}(^1\text{D})$ atom and agrees with previous results from our laboratory.

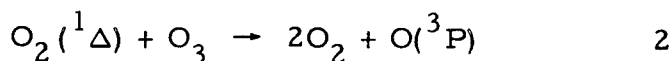
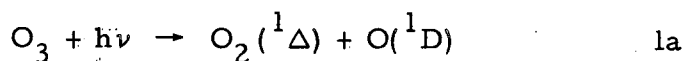
INTRODUCTION

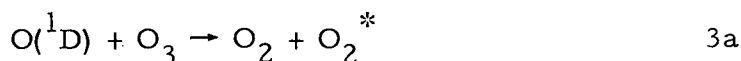
The photolysis of O_3 is the most important photochemical process in the upper atmosphere below about 70 km. Not only is the primary photodecomposition efficiency equal to one, but both the O_2 and O fragments are electronically excited. Therefore it is important to understand the primary process in detail.

Dry Ozone

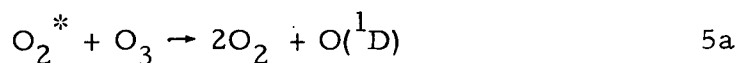
The photolysis of O_3 has been studied for a long time. The results to 1930 were summarized by Schumacher.¹ In the 1930's the problem was again examined by Heidt and Forbes.²⁻⁴ In dry O_3 , the photolysis was studied at 2080, 2540, and 2800 Å in the presence of O_2 at total pressures of 230-620 torr and partial pressures of 35-430 torr and 15-585 torr for O_3 and O_2 , respectively.³ In some cases the quantum yield for O_3 disappearance was as high as 6.7, indicating that an energy chain must be present.

This problem then lay dormant for over two decades, until McGrath and Norrish^{5,6} examined the flash photolysis. In their first paper⁵ they used kinetic spectroscopy and observed large amounts of vibrationally excited O_2 in its ground electronic state, $^3\Sigma_g^-$, with $v \leq 17$. In their second paper,⁶ they added H_2O vapor and found that the vibrationally excited O_2 could be completely suppressed and replaced by HO radicals. Combining their observations with those of Heidt and Forbes they proposed the now well-known mechanism for O_3 photodecomposition.





The efficiency of reaction 1a was not known, and possibly $\text{O}_2(^3\Sigma_g^-)$, $\text{O}_2(^1\Sigma_g^-)$, and $\text{O}(^3\text{P})$ were also produced in that reaction. They believed that O_2^* formed in reaction 3a was the vibrationally excited O_2 which they had observed, and that it carried the energy chain via



It is not clear that their experiments prove that the chain carrier O_2^* formed in reaction 3a is vibrationally excited O_2 , since their experiments were performed in a large excess of N_2 which has since been shown to be an efficient deactivator for $\text{O}(^1\text{D})$, converting it to $\text{O}(^3\text{P})$.⁷⁻¹² The vibrationally excited O_2 may come from reaction 4, which is known from the visible photolysis of O_3 to not propagate chains.^{13, 14}

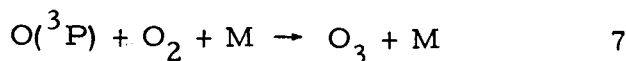
Conclusive evidence that $\text{O}(^1\text{D})$ was produced came from the observation of HO radicals in the experiments in the presence of H_2O vapor, since $\text{O}(^3\text{P})$ does not have sufficient energy to react with H_2O to produce HO. Because the vibrationally excited O_2 could be eliminated completely in the presence of H_2O , it can be inferred that H_2O efficiently deactivates vibrationally excited O_2 . The work of DeMore and Raper^{7, 15} showed that the efficiency of $\text{O}(^1\text{D})$ production in reaction 1 was 1.0 for photolysis at wavelengths $<3000 \text{ \AA}$.

In 1965, Norrish and Wayne¹⁶ published their studies on the continuous low intensity photolysis at 2537 \AA of dry O_3 at 2-50 torr. They

found that at high pressures the quantum yield of O_3 decomposition, $-\Phi\{O_3\}$, rose to as high as 16.7 (at 50 torr O_3). There was no effect of absorbed intensity, but different results were obtained in two different cells which suggested the presence of wall reactions. In both cells the low-pressure extrapolated value of $-\Phi\{O_3\}$ was near 4.0. Thus they concluded that with the addition of a wall terminating step for O_2^*



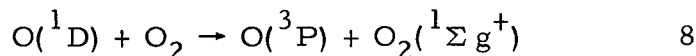
their results were consistent with the McGrath and Norrish mechanism. In the presence of N_2 or CO_2 , the limiting quantum yield for O_3 disappearance at high pressures of added gas, $-\Phi_\infty\{O_3\}$, approached two, which would be expected if the added gas quenched both $O(^1D)$ and $O_2(^1\Delta)$. With added O_2 , $-\Phi_\infty\{O_3\}$ approached zero which was expected since O_2 can quench $O(^1D)$ and react with $O(^3P)$



At this point the problem appeared solved except for the details. It was still necessary to determine the efficiency of $O_2(^1\Delta)$ production, or if $O_2(^1\Sigma_g^+)$ was produced in reaction 1. Also the nature of O_2^* and the efficiency of its production were still unknown.

Soon, however, discrepancies appeared. The first anomaly concerned the fate of $O_2(^1\Delta)$. That it can react with O_3 via reaction 2 had been established and the rate constant determined.¹⁷ Subsequent investigations¹⁸⁻²¹ have confirmed the reaction. Though the rate constant is not large, it is still large enough to completely consume all the $O_2(^1\Delta)$. The reactivity of $O_2(^1\Delta)$ with N_2 or CO_2 is negligible,^{22, 23} and these molecules could not possibly quench the reaction and drop $-\Phi\{O_3\}$ to 2.0.

Possibly the discrepancy could be explained by the formation of $O_2(^1\Sigma g^+)$ rather than $O_2(^1\Delta)$ in reaction 1. Evidence for this possibility was put forth by Izod and Wayne.²⁴ Though they detected the emission from $O_2(^1\Delta)$ at 1.27μ in the photolysis of O_3 , they argued that it arose from the secondary reaction of $O(^1D)$ with O_2 , since they could only see the signal in the presence of O_2 . No $O_2(^1\Delta)$ was detected when N_2 or Ar replaced O_2 . That $O_2(^1\Sigma g^+)$ reacts readily with O_3 had been established,¹⁸ and subsequently confirmed.²⁵ However, again the reactivity of $O_2(^1\Sigma g^+)$ with N_2 or CO_2 is much too slow to have permitted quenching by these gases.^{11, 26} Furthermore, Gauthier and Snelling,²⁷ as well as Gilpin et al.,²⁸ have shown that at 2537 Å (Gilpin et al. used radiation between 2375 and 2625 Å) only $O_2(^1\Delta)$ is produced in reaction 1 (<5% $^1\Sigma g^+$) and that the $O_2(^1\Sigma g^+)$, but little or none of the $O_2(^1\Delta)$, comes from the interaction of $O(^1D)$ with O_2 in conformance with Noxon's findings.²⁹



Wayne has also come to this conclusion in more recent work.³⁰

Further experiments were done by Wayne and White,³¹ who studied the photolysis in a flow system at O_3 pressures less than one torr. They only obtained relative quantum yields, but they found that these dropped by a factor of 5 as the O_3 pressure was reduced from 0.67 to 0.10 torr. Wayne has privately informed us that these observations were incorrect.

Jones and Wayne³² rechecked the results of Norrish and Wayne at 2537 Å and corroborated the earlier findings. Jones and Wayne also examined the photolysis at 3130 and 3340 Å, where there is insufficient energy to produce both $O(^1D)$ and $O_2(^1\Delta)$. Since $-\Phi\{O_3\}$ was still about 4.0, the products of reaction 1 must have been $O(^3P)$ and singlet O_2 . (At 3130 Å, there is sufficient thermal energy to produce $O(^1D)$ about 10% of the time, and $-\Phi\{O_3\}$ is slightly greater than 4.0.) At about the same time, more extensive studies of Castellano and Schumacher³³ indicated the same results at 3130 Å for short irradiation times.

Jones, Kaczmar, and Wayne³⁴ returned to the flow system and photolyzed dry O_3 at 2537 Å in the presence of 10-90% O_2 at total pressures of 0.1 to 2 torr. The O_3 pressures were between 0.05 and 2 torr, and in these experiments $-\Phi\{O_3\}$ was close to 4 independent of either the O_3 or O_2 pressure. (Actually $-\Phi\{O_3\}$ was 4.5 with 10% O_2 and this dropped to 3.5 with 90% O_2 .) Presumably under these conditions, reaction 5a is unimportant compared to reaction 6, and the results conform to those in a static system at low pressure.

Finally Jones and Wayne³⁵ extended the measurements to six wavelengths between 2480 and 3340 Å. The quantum yield of O_3 consumption increased with the O_3 pressure as at 2537 Å. A long extrapolation of rather scattered data indicated a low-pressure intercept of 4.0 in each case. At 3340 Å, some experiments were done with H_2 added to test for the presence of $O(^1D)$, since $O(^1D)$ reacts with H_2 to give a long chain decomposition of O_3 . The experiments confirmed that only $O(^3P)$ was produced at this wavelength.

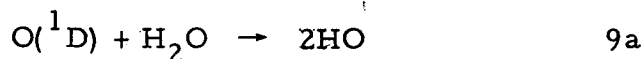
At about the time that our experiments were initiated, a paper appeared by Webster and Bair³⁶ which cast doubt on some aspects of the

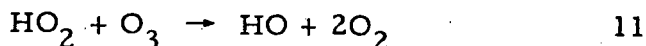
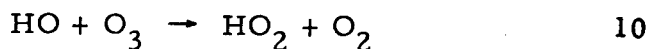
McGrath-Norrish mechanism. Webster and Bair photolyzed 0.2 torr of O_3 in a static system with steady illumination at 2537 Å. They worked at very low decomposition (0.5-1%), and only measured relative quantum yields. They found that the addition of N_2 reduced $-\Phi\{O_3\}$, as had Norrish and Wayne.¹⁶ However, realizing that N_2 could not quench $O_2(^1\Delta)$, they assumed that $-\Phi_{\infty}\{O_3\} = 4.0$, rather than 2.0 found by Norrish and Wayne. In the absence of N_2 , $-\Phi\{O_3\}$ would then be ~ 5.0 . The addition of He, which does not quench $O(^1D)$,³⁷⁻³⁹ raised the yield slightly to about 50% greater than that in excess N_2 . From these results Webster and Bair concluded that O_2^* did not undergo reaction 5a, but rather that O_2^* was really two $O(^3P)$ atoms. The enhancement effect of He was then to minimize loss of $O(^3P)$ on the wall. Because of the long lifetime needed for O_2^* , ($\tau > 10^{-3}$ sec), the $^3\Sigma_u^-$ and $^3\Sigma_u^+$ states of O_2 were excluded as possibilities.

Wet Ozone

It was Warburg⁴⁰ who first found that the photodecomposition of O_3 was enhanced in the presence of water. Forbes and Heidt² made a quantitative study with radiation at 2800, 2540, and 2100 Å and O_3 pressures between 10 and 760 torr. They found that $-\Phi\{O_3\}$ could rise to as high as 130, and that it was proportional to $[H_2O]$ and dropped as the absorbed intensity, I_a , was raised. The intensity effect suggests a radical-radical termination step, but Norrish and Wayne⁴¹ found little change in $-\Phi\{O_3\}$ with intensity and concluded that radical-radical termination was unimportant.

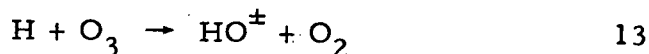
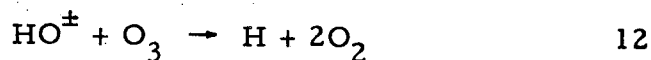
McGrath and Norrish^{6, 42} demonstrated the presence of HO radicals in the flash photolysis and proposed the following steps to propagate the chain





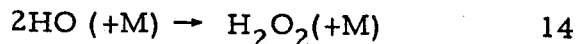
In further experiments Basco and Norrish⁴³ demonstrated that up to 2 quanta of vibrational energy could be present in the HO radical.

It was DeMore⁴⁴ who pointed out, from a comparison with Kaufman's results,⁴⁵ that reactions 10 and 11 were unsatisfactory. DeMore proposed that the chain steps were

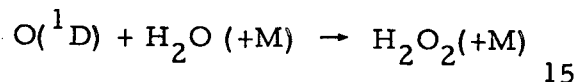


where HO^\pm is vibrationally excited HO. Support for this hypothesis was soon given⁴⁶ in the liquid phase photolysis of O_3 at -186°C . The addition of O_2 suppressed the chain indicating that O_2 scavenged the H atoms and that HO_2 did not react with O_3 , at least at low temperatures in the liquid phase. Confirmation that $\text{HO}^\pm(v=9)$ formed in reaction 13 reacted rapidly with O_3 was given by Potter et al.⁴⁷

Recent flash photolysis studies^{48, 49} have shown that $-\Phi\{\text{O}_3\}$ is not increased in the presence of water vapor and that $\text{HO}(v=0, 1)$ is essentially uncreative to O_3 . Thus it is not clear how the chains are initiated in the steady illumination experiments. Langley and McGrath⁴⁹ have suggested that some H_2O_2 might be produced via



and that the reaction of $\text{O}(^1\text{D})$ with H_2O_2 would produce $\text{HO}(v=3)$ to start the chain. Another possible route to H_2O_2 production is direct insertion



Present Status

At present the O_3 photolysis can be summarized as follows. The initial photodecomposition proceeds with unit efficiency. For wavelengths below 3000 Å, $O(^1D)$ is the exclusive O-atom product; at 3340 Å, $O(^3P)$ is the exclusive O-atom product; and at 3130 Å, $O(^3P)$ is the main O-atom product ($\geq 90\%$). At 3130 and 3340 Å, singlet O_2 is produced, but it may be either $O_2(^1\Delta)$ or $O_2(^1\Sigma g^+)$. At lower wavelengths, only $O_2(^3\Sigma g^-)$ or $O_2(^1\Delta)$ is energetically possible until wavelengths < 2660 Å are reached; then $O_2(^1\Sigma g^+)$ could also be produced, though it apparently is not at 2537 Å. Recent absolute measurements for $-\Phi\{O_3\}$ below 3100 Å are those of Wayne and his coworkers, who found $-\Phi\{O_3\} = 2.0$ in the presence of a large excess of CO_2 or N_2 . However, this value was obtained for extended conversions so that reaction 7 may be playing a role.

Singlet O_2 (either $^1\Delta$ or $^1\Sigma g^+$) is removed exclusively by reaction with O_3 , and $O(^3P)$ can be removed either by reaction 4 or 7. The nature of O_2^* formed in reaction 3a, the efficiency of its formation, and its fate are not established.

In the presence of H_2O the photodecomposition is enhanced and proceeds by a long chain process, presumably involving reactions 12 and 13. However, the chain initiating and terminating steps have not yet been found to be satisfactory in explaining all the data.

We have undertaken a re-examination of the steady-state photolysis of O_3 in order to:

- 1) Determine the efficiency of singlet O_2 production in reaction 1 as a function of exciting wavelength,

- 2) Determine the efficiency of O_2^* production in reaction 3a and the fate of O_2^* ,
- 3) Study some quenching reactions of $O(^1D)$ with various gases as a function of exciting wavelength,
- 4) Help elucidate the chain mechanism in the presence of H_2O vapor, and
- 5) Study the photolysis in the presence of N_2O .

EXPERIMENTAL

A conventional high-vacuum line utilizing Teflon stopcocks with Viton "O" rings was used. Both mercury and stopcock grease were rigorously excluded. Pressures were measured with a sulfuric acid manometer, a NRC alphanatron gauge or a Veeco thermocouple gauge. Pressures of O_3 lower than 100μ were measured by expanding a higher pressure into a calibrated volume. Ozone was always measured with the sulfuric acid manometer and was never introduced into either the alphanatron or the thermocouple gauge. When ozone was added as a second gas into the reaction cell, its concentration was determined from its optical absorption. Calibration curves of light absorption vs. ozone pressure were made at all wavelengths. At 2537 A, Beer's law was obeyed and the extinction coefficient agreed with that in the literature.⁵⁰ At 2288 and 2800 A, the irradiation was not monochromatic and the Beer's law plots were curved. Concentrations were determined from these plots directly.

The reaction cell was a cylindrical quartz cell 10 cm long and 5 cm in diameter. During a run the ozone concentration was monitored continuously from its light absorption. To obtain the rate of photodecomposition for low conversions, a method utilizing the simultaneously measured difference between the incident and transmitted radiation was employed. It permitted determination of decomposition rates at conversions of $<1\%$. Dark decomposition of the ozone, as well as changes of concentration due to mixing, were negligible under all the conditions employed.

The wavelengths of the irradiation were obtained by use of:

2288 A: A Phillips Cd resonance lamp Typ. 93107E plus a chlorine gas filter (300 torr and 5 cm in length) to remove radiation >3000 A

and a Corning 9-30 filter to remove radiation below 2200 Å.

In addition to the 2288 Å line, the weaker 2265 Å line was also passed.

2537 Å: A Hanovia flat-spiral low-pressure Hg resonance lamp Model No. Z1400-013 plus the chlorine and Corning 9-30 filters, as well as a Corning 7-54 filter which only passes radiation between 2300 and 4200 Å.

2800 Å: A high pressure 150 watt Osram xenon arc lamp with a Jarrell-Ash 1/4-meter Ebert monochromator, Model 82-410 with 2 mm slit widths. The band pass at 1/2-height was about 100 Å.

Actinometry was done at each wavelength by measuring the amount of products obtained when substances of known behavior were photolyzed under similar conditions. In all cases the light absorption was matched to that in the corresponding O_3 photolysis. At 2288 and 2537 Å, HBr was used. Its photolysis gives H_2 with a quantum yield of one.⁵¹ At 2800 Å, HI was used. It was assumed that $-\Phi\{H_2\}$ was unity, as it is at lower wavelengths.⁵²

Ozone was prepared by passing an electric discharge through Air Products Research Grade O_2 . The O_3 produced was collected at $-196^\circ C$, and the excess O_2 pumped away. The O_3 was then distilled at $-186^\circ C$, stored at $-196^\circ C$, and degassed at this temperature before each run. Matheson N_2O and Bone Dry CO_2 were distilled trap to trap, the medium fractions being retained. Air Products Research Grade N_2 and Matheson He

were used without purification. Both distilled H_2O and tap water were used after degassing at -50°C . The results were similar with either source of H_2O . The actinometer gases were Matheson HBr and HI which were distilled at -100°C to remove the corresponding halogen and degassed at -196°C before use.

PHOTOLYSIS OF DRY OZONE

Results

Pure dry O_3 was photolyzed at 2800, 2537, and 2288 Å. At each wavelength, the pressure of O_3 was used which gave the maximum change in percent transmission of the radiation for a given percent decomposition. Initially the quantum yields of O_3 removal were irreproducible. Only after conditioning the reaction vessel by several photolyses of pure dry O_3 to high conversions could reproducible results be obtained. For example, after introducing HBr to the reaction cell, values of $-\Phi\{O_3\}$ as high as 15 were obtained even after prolonged pumping of the cell to pressures below 1μ . A similar effect was observed after baking the reaction cell.

For photolyses to low conversions ($< 3\%$) in the conditioned cell in the absence of any added gas the resultant quantum yields, $-\Phi_o\{O_3\}$, are listed in Table I. At all the wavelengths, $-\Phi_o\{O_3\}$ is measurably greater than 4, being 5.8 ± 0.3 , 5.0 ± 0.3 , and 5.9 ± 0.3 for radiation at 2800, 2537, and 2288 Å, respectively. The runs at 2537 Å were with the lowest O_3 pressure, and some wall deactivation could have occurred, accounting for the somewhat lower value at that wavelength.

Experiments were then done with the same pressures of O_3 , but with either CO_2 or N_2 added. The results for low conversions at 2800, 2537, and 2288 Å, are shown in Figs. 1-4. The addition of either gas reduces $-\Phi\{O_3\}$ to a limiting value, $-\Phi_\infty\{O_3\}$, of about 4.0; the exact values are listed in Table I. The addition of 13 torr of He in the CO_2 experiments at 2537 Å had no noticeable effect. The only other absolute measurement of these values was made by Norrish and Wayne,¹⁶ who found values of

about 2.0. At that time they explained these low values as resulting from the quenching of singlet O_2 by CO_2 and N_2 . It is now known that this explanation cannot be correct (see Introduction), and the low value is inconsistent with any proposed mechanism for O_3 photodecomposition. The reason for the low values found by Norrish and Wayne is that in their work the percent decomposition of the O_3 was considerably larger than in our work. Thus considerable O_2 was present, reaction 7 was important, and $-\Phi_{\omega}\{O_3\}$ was reduced. That their percent decomposition was excessive can be deduced from the half-quenching pressures of CO_2 and N_2 required. (They do not report the percent decomposition in their paper.) Their half-quenching pressures were much too large to be consistent with the now-known values for $O(^1D)$ deactivation (See below). To check the above argument, we performed experiments with excess CO_2 for extended conversions at 2537 Å and found that $-\Phi_{\omega}\{O_3\}$ could be considerably reduced below 4.0.

The investigations of both Norrish and Wayne¹⁶ and Webster and Bair³⁶ show that $-\Phi_o\{O_3\}$ is greater than $-\Phi_{\omega}\{O_3\}$, in concordance with our findings. Webster and Bair report $-\Phi_o\{O_3\} = 4.9$ at 2537 for $[O_3] = 0.20$ torr based on $-\Phi_{\omega}\{O_3\} = 4.0$. This result agrees exactly with ours. The addition of excess He [which does not quench $O(^1D)$] raised the value to 6.0 in Webster and Bair's work, but the addition of 13 torr of He only raised our value by 6%. However the experimental uncertainties in both measurements are such that this discrepancy is not alarming. (Actually as we shall show, in excess He the value should be 5.5 ± 0.3 .)

Further substantiation that $-\Phi_o\{O_3\}$ is greater than 4.0 comes from the work of Heidt and Forbes.³ Their results, which were obtained in the

presence of O_2 , are plotted in Fig. 5 vs. the ratio $[O_2][M]/[O_3]$. The abscissa is the parameter which determines the relative importance of reactions 7 and 4. At high values of the abscissa, reaction 7 is important, and $-\Phi\{O_3\}$ is as low as 2.3. However, as reaction 7 becomes less important, $-\Phi\{O_3\}$ rises; the value of $-\Phi\{O_3\}$ extrapolated to $[O_2][M]/[O_3] = 0$ is in good agreement with ours, though the Heidt and Forbes data are badly scattered.

The flow experiments of Jones et al.³⁴ done at 2537 Å give $-\Phi_O\{O_3\} = 4.5 \pm 0.3$ for mixtures of 10% O_2 , and lower values for mixtures with a higher percentage of O_2 . In the latter case the reduced values can be accounted for by reaction 7. The value of 4.5 ± 0.3 , which does not include a stated 10% uncertainty in actinometry, in the former case is not significantly below the value of 5.0 ± 0.3 obtained by us.

The only studies which indicate that $-\Phi_O\{O_3\}$ is 4.0 at low O_3 pressures are those of Wayne and his coworkers^{16, 32, 35} done at 2537 Å in a static system with steady illumination. However, this conclusion is based on a long extrapolation from high-pressure results carried out to extended conversions. Furthermore there are other problems in these studies (see below). We conclude that the conclusion that $-\Phi_O\{O_3\}$ is 4.0 can be discounted.

The pressure dependence of $-\Phi_O\{O_3\}$ was determined in a series of runs at several wavelengths. For these runs $-\Phi_\infty\{O_3\}$ was assumed to be 4.0 in the presence of CO_2 , and the values of $-\Phi_O\{O_3\}$ are based on this assumption. The results are shown in the semi-log plot, Fig. 6.

For pressures between 0.4 and 2.7 torr, $-\Phi_O\{O_3\}$ is invariant at 5.5 ± 0.3 to pressure changes or to the wavelength of the incident radiation between 2288 and 2850 Å. Baking (followed by conditioning) the

cell or adding 5μ of H_2O vapor also had no effect. Experiments at pressures between 0.1 and 0.3 torr were done at 2537 Å. The results are more scattered and $-\Phi_{\text{O}}\{\text{O}_3\}$ varies from 4.5 to 5.6. At these low pressures some wall deactivation, which may vary from run to run, possibly occurs, accounting for both the scatter and the fall-off in $-\Phi_{\text{O}}\{\text{O}_3\}$.

Finally the effect of absorbed intensity, I_a , was investigated, and the results are in Table II. A 430-fold variation in I_a had no effect in agreement with the findings of Norrish and Wayne.¹⁶

It is clear that $-\Phi_{\text{O}}\{\text{O}_3\} = 5.5 \pm 0.3$ at low conversions for O_3 pressures between 0.4 and 2.7 torr. In the absence of wall deactivation, it seems likely that this value is valid to O_3 pressures of 0.1 torr or even lower. The possibility that this value is high because of the presence of H_2O vapor, which greatly enhances the quantum yield, can be discounted for three reasons: 1) baking the cell (and then conditioning it by photolyzing dry O_3) or adding trace amounts of H_2O vapor had no effect, 2) there is no effect of O_3 pressure, though later we will show that in the presence of H_2O , changing the O_3 pressure does change the results, and 3) there is no effect introduced by changing I_a , though in the presence of H_2O vapor a significant change results by altering I_a (see later results).

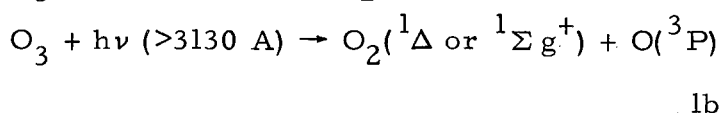
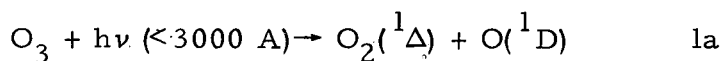
The results of Wayne et al.^{16, 32, 35} indicate that for O_3 pressures above 2 torr, $-\Phi_{\text{O}}\{\text{O}_3\}$ increases dramatically, reaching values of 16.7 at 50 torr. Perhaps there is a dramatic shift in the O_3 photodecomposition mechanism at O_3 pressures of 2-3 torr. This seems unlikely to us. Furthermore, Heidt and Forbes³ performed experiments at O_3 pressures up to 428 torr at 0°C and up to 294 torr at room temperature, and except for two points which gave values for $-\Phi\{\text{O}_3\} = 6.7$ and 6.3, they found

that $-\Phi\{\text{O}_3\}$ was always less than 6.0. Never did they find values even approaching those reported in the Wayne studies.

We suggest that the large values for $-\Phi\{\text{O}_3\}$ found in the Wayne studies may be incorrect, possibly because the reaction cell was not properly conditioned. Effects similar to those observed by us after HBr had been present (i. e. $-\Phi\{\text{O}_3\} \sim 15$) might have occurred in the Wayne studies. Excessive baking of the cell likewise produces high quantum yields. Evidence for this hypothesis comes from the work of Norrish and Wayne¹⁶ in which $-\Phi\{\text{O}_3\} < 5$ even for $[\text{O}_3] = 17$ torr in a 4-cm diameter cell, but $-\Phi\{\text{O}_3\} \sim 8.0$ in a 7-cm diameter cell at the same pressure. Presumably the 7-cm diameter cell was not properly conditioned. It should be emphasized, however, that the pressure ranges used by us and in the Wayne studies barely overlapped, and that there is no direct discrepancy in experimental results at the pressures used in both studies.

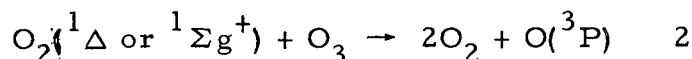
Mechanism

The primary photochemical act is

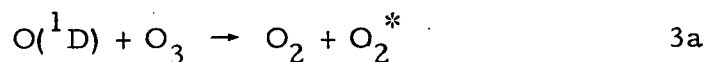


For radiation between about 3000 and 3130 Å, both processes 1a and 1b can occur, with reaction 1b occurring about 40% of the time at about 3100 Å.¹⁵ Singlet O_2 is produced exclusively at all wavelengths. For process 1a, only $\text{O}_2(^1\Delta)$ is energetically possible for radiation > 2660 Å. With radiation at 2537 Å, $\text{O}_2(^1\Delta)$ is certainly the dominant, if not the exclusive, state of O_2 .^{27, 28} At wavelengths below 2537 Å it is not known whether some $\text{O}_2(^1\Sigma_g^+)$ is formed. However, its presence would not affect any of the following arguments, so we will ignore this possibility.

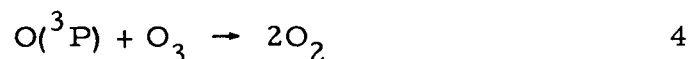
The singlet O_2 is always removed via reaction with O_3



In the absence of added gases $O(^1D)$ reacts with O_3

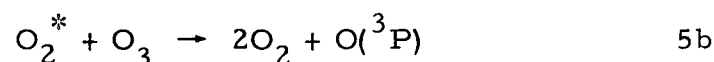
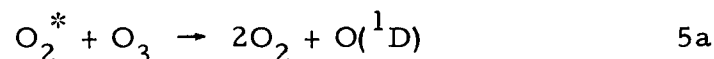


where O_2^* is some unspecified excited electronic state of O_2 (or 2 $O(^3P)$ atoms). In the absence of significant amounts of O_2 , i. e. at low conversions, the $O(^3P)$ atom is removed in the well-known reaction



Otherwise reaction 7 must also be involved.

Before estimating the relative importance of reactions 3a or 3b, let us examine the fate of O_2^* . There are three possible reactions



Reaction 5a can be eliminated from a consideration of the results of Goldman et al.⁵³ They studied the photolysis of O_3 in the presence of N_2O and measured the N_2 produced. Their results showed that $O(^1D)$ was not regenerated via reaction 5. At the time they accepted reaction 5a and concluded that O_2^* must have been deactivated completely by small amounts of N_2O . However, our work with N_2O , soon to be discussed,

shows that in fact this is not so. Therefore reaction 5a is negligible. Gilpin et al.²⁸ have also reported that <10% of the O(¹D) can come from chain regeneration. At very low pressures reaction 6 may play some role, but it certainly is unimportant at pressures above 0.4 torr; reaction 5b is the dominant fate of O₂^{*}.

The mechanism consisting of steps 1a, 2-4, and 5b predicts that

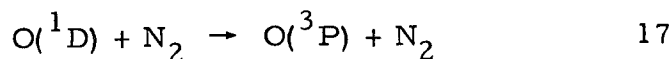
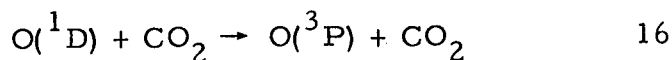
$$-\Phi_o\{O_3\} = 4 + 2k_{3a}/k_3 \quad I$$

where $k_3 \equiv k_{3a} + k_{3b}$. Since $-\Phi_o\{O_3\} = 5.5 \pm 0.3$, then $k_{3a}/k_3 = 0.75 \pm 0.15$.

The nature of O₂^{*} is of considerable interest. Webster and Bair³⁶ argued against O₂(³Σu⁺ or ³Σu⁻). They favored the explanation that O₂^{*} was in reality two O(³P) atoms, and this possibility must be given serious consideration. As far as we know neither O₂(¹Δ) nor O₂(¹Σg⁺) is deactivated at the wall, and these possibilities for O₂^{*} are not likely. A more compelling (but not conclusive) argument against O₂(¹Δ) or two O(³P) atoms is the fact that $-\Phi_o\{O_3\}$ does not fall below 4.0 even at 0.1 torr pressure, as would be expected for complete removal at the wall. (In fact $-\Phi_o\{O_3\}$ does not fall below 4.5.) Evidence against O₂(¹Σg⁺) comes from the work of Gauthier and Snelling²⁷ and Gilpin et al.²⁸ who showed that all the O₂(¹Σg⁺) could be explained by reaction 8. Consequently we feel that the most likely candidates for O₂^{*} are O₂(¹Σu⁻) or O₂(³Δ_u). The production of O₂(¹Σu⁻) violates the spin conservation rules (which may or may not apply), but the production of O₂(³Δ_u) is spin allowed. The precise identification of O₂^{*} will require more work.

Deactivation of O(¹D)

In the presence of CO₂ or N₂, the O(¹D) atom can be deactivated



These reactions account for the drop in $-\Phi\{\text{O}_3\}$ with the addition of these gases for then reaction 3a is reduced. When $-\Phi\{\text{O}_3\} = -(\Phi_0\{\text{O}_3\} + \Phi_\infty\{\text{O}_3\})/2$, then $k_3[\text{O}_3] = k_{16}[\text{CO}_2]$ or $k_{17}[\text{N}_2]$. From the decay curves in Figs. 1-4, the values for k_{16}/k_3 and k_{17}/k_3 can be obtained and they are listed in Table III. The data in the figures are rather badly scattered, especially for N_2 at 2537 Å, so that these determinations are not very accurate.

The only direct determination of k_{17}/k_3 was made by Snelling and Bair⁹ in the flash photolysis of O_3 . They report a value of 0.065 ± 0.03 in reasonable agreement with our values. The later "corrected" value of 0.50 ± 0.25 of Biedenkapp and Bair⁵⁴ is presumably incorrect, since the value they obtain for k_3 is much lower than obtained by others.^{28, 53}

There appears to be no direct measurement of k_{16}/k_3 . However, there are many studies from which k_{17}/k_{16} can be deduced, and these results are listed in Table IV. Except for two values obtained in the photolysis of O_2 at 1470 Å, all the other values lie between 0.17 and 0.35 even though the experimental conditions and the translational energy of $\text{O}(^1\text{D})$ was considerably different in the different experiments.

PHOTOLYSIS OF WET OZONE

Results

We measured $-\Phi \{O_3\}$ in the presence of H_2O under different conditions of pressure, wavelength, and light intensity. In these experiments all quantum yields were based on $-\Phi_{\infty} \{O_3\} \approx 4.0$ in excess CO_2 in the absence of H_2O . The data are in Table V. For a number of experiments a third gas, either CO_2 or He, was added, either after determining $-\Phi \{O_3\}$ or in a separate experiment, and the quantum yield of O_3 disappearance (designated $-\Phi' \{O_3\}$) again measured. Those experiments in which the third gas was added after the original determination gave the same results as when a fresh unphotolyzed mixture was used. The advantage of a fresh mixture is that no O_2 is present, but the advantage of adding the third gas after the original photolysis is that a direct comparison of the change in $-\Phi \{O_3\}$ can be made.

The most obvious effect is that $-\Phi \{O_3\}$ increases with the ratio $[H_2O]/[O_3]$, reaching a maximum value of about 19 at $[H_2O]/[O_3] \sim 2$ and $[O_3] = 1.1$ torr. Further increases in $[H_2O]/[O_3]$ cause a drop in $-\Phi \{O_3\}$. This effect is most easily seen in Fig. 7 in which $-\Phi \{O_3\}$ is plotted vs. $[H_2O]^{1/2}$ for runs at 2800 Å with $I_a \approx 3 \mu/\text{min}$ and $[O_3] = 1.1$ torr. At low H_2O vapor pressures $-\Phi \{O_3\}$ increases linearly with $[H_2O]^{1/2}$ in agreement with the observations of Forbes and Heidt.² A maximum value of about 18 is reached at $[H_2O]^{1/2} = 1.5 \text{ torr}^{1/2}$, and then $-\Phi \{O_3\}$ falls slightly with further increases in $[H_2O]$.

The maximum value of $-\Phi \{O_3\}$ also seems to increase with $[O_3]$, at least at lower O_3 pressures, but this effect is not very marked, perhaps because $[O_3]$ was only varied by a factor of 10.

The effect of I_a on $-\Phi \{O_3\}$ was studied at 2537 Å, $[O_3] = 0.18$ torr, and $[H_2O]/[O_3] = 2.0$. A 60-fold drop in I_a raises $-\Phi \{O_3\}$ from 4.9 to 9.7, again in accord with the findings of Forbes and Heidt.² The results appear to be similar at all wavelengths, and the addition of excess He only raised $-\Phi \{O_3\}$ slightly.

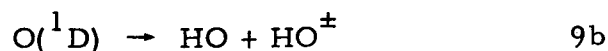
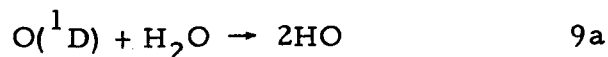
The effect of adding CO_2 is to repress $-\Phi \{O_3\}$, and eventually drop it to 4.0. However, the $[CO_2]/[H_2O]$ ratio needed to reduce the chain component of $-\Phi \{O_3\}$ (i. e. $-\Phi \{O_3\} = 4.0$) to one-half its value is much greater than the $[CO_2]/[O_3]$ ratio necessary to produce the same effect when H_2O is omitted.

Finally one experiment was done with H_2 instead of water vapor. The conditions were 0.18 torr O_3 , 12 torr H_2 , $\lambda = 2537$ Å, and $I_a = 13$ μ /min. The quantum yield of O_3 disappearance was 103, which agrees with the large quantum yields found by others,^{41, 46} though our value is considerably larger.

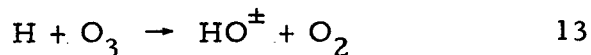
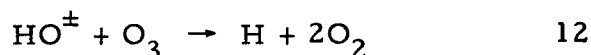
One explanation for the discrepancy between the low-intensity steady illumination data and the high-intensity flash photolysis data is that H_2O_2 is formed and it initiates the chain step in the low intensity experiments.⁴⁹ To check this possibility we carefully looked for induction periods in our O_3 decay curves. Our results show no induction times, the slopes of the decay curves being independent of conversion even at conversions lower than 0.5%. In a typical run (0.5 torr H_2O , 0.5 torr O_3 , $-\Phi \{O_3\} = 20$), the total H_2O_2 produced must be $\leq 2 \times 10^{-4}$ torr at 0.5% conversion. It is difficult to believe that this small amount of H_2O_2 could successfully compete with H_2O for the $O(^1D)$ atom to initiate the chains when 12 torr of H_2 produces chain lengths of only 130 or less.

Mechanism

In the presence of water vapor, the $O(^1D)$ atom can react with H_2O

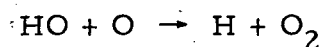


where HO^\pm is vibrationally excited HO with sufficient energy ($v \geq 2$) to initiate the chain



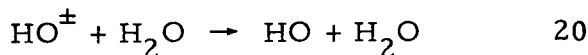
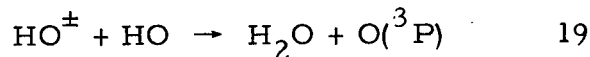
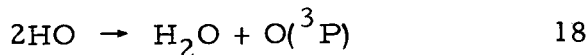
In reaction 9b there is sufficient energy to produce HO ($v = 2$) and if the excess translational energy of the $O(^1D)$ atom is considered, even HO ($v = 3$). The HO radical with $v = 2$ has been observed by Basco and Norrish.⁴³ In reaction 13 the HO radical produced can have $v \leq 9$. The reactivity of HO^\pm probably depends on its vibrational energy. However, for simplicity we shall assume that for $v \geq 2$, all the HO^\pm are indistinguishable.

The chain initiation step important in the presence of large concentrations of O atoms

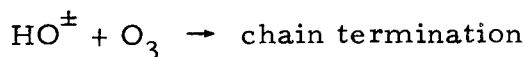


cannot be important here, as pointed out by DeMore.⁴⁴ Also in the flash photolysis, where the O atom concentration is even higher, the water-induced chain does not occur.^{48, 49} We have attempted to fit several mechanisms utilizing the above reaction as a chain initiator, but each has led to a rate law inconsistent with our observations in one way or another.

The radical removal steps are



A number of possible chain terminating reactions have been omitted for the following reasons. The excited radical HO^\pm might have been removed by



The former reaction undoubtedly occurs, but since $[\text{HO}^\pm] \ll [\text{HO}]$, it is negligible compared to reaction 19. The latter reaction is only a formalism, since for kinetic purposes HO^\pm is defined as only those HO radicals that produce H atoms when interacting with O_3 (all the HO radicals with $v \geq 2$ may not be HO^\pm). Wall deactivation steps have been omitted since they must be diffusion controlled, and the addition of excess He only introduces a slight increase in $-\Phi\{\text{O}_3\}$. Some wall deactivation may be occurring, but it cannot be the dominant chain-termination step. The possibility that the H atom reacts with O_3 to terminate the chain, viz



has also been ignored. It cannot be the major chain termination step, since it would lead to a rate law in which $-\Phi\{\text{O}_3\}$ would decrease with an increase in $[\text{O}_3]$, contrary to our findings.

The mechanism consisting of reactions 1a, 2-4, 5b 9a, 9b, 12, 13 and 18-20 leads to the rate law

$$-\Phi \{O_3\} = 3 + \alpha + (2k_{3a} + k_{3b})[O_3]/(k_3[O_3] + k_9[H_2O]) + \frac{2(k_{9b}/k_9)k_{12}[O_3]\beta}{k_{19}(I_a\beta/k_{18})^{1/2} + k_{20}[H_2O]} \quad \text{II}$$

where

$$\alpha \equiv (k_{3a}[O_3] + k_9[H_2O])/(k_3[O_3] + k_9[H_2O]) \quad \text{III}$$

and

$$\beta \equiv k_9[H_2O]/(k_3[O_3] + k_9[H_2O]) \quad \text{IV}$$

In deriving the rate law II, it was assumed that $[HO^\pm] \ll [HO]$, so that reaction 9b and 19 do not significantly influence the steady-state value of $[HO]$. The quantity α varies between 0.75 and 1.0, and is essentially a constant.

The last term in Eqn. II is the dominant one in determining the change in $-\Phi \{O_3\}$ when H_2O is added. At low H_2O pressures, $k_{20}[H_2O] < k_{19}(I_a\beta/k_{18})^{1/2}$, and this term reduces to

$$\frac{2k_{9b}k_{12}[O_3]}{k_9k_{19}} \left[\frac{k_9k_{18}[H_2O]}{I_a(k_3[O_3] + k_9[H_2O])} \right]^{1/2}$$

This expression predicts that the increase in $-\Phi \{O_3\}$ will be inversely proportional to $I_a^{1/2}$; directly proportional to $([H_2O][O_3])^{1/2}$ at low values of $[H_2O]/[O_3]$; and directly proportional to $[O_3]$, but independent of

$[H_2O]$, at high $[H_2O]/[O_3]$. At high H_2O pressures, $k_{20}[H_2O]$ is no longer negligible, and an increase in $[H_2O]$ reduces $-\Phi\{O_3\}$. All of these predictions conform to our findings and to the observation that no measurable chain occurs in the flash photolysis, where I_a is very large.

Though the mechanism leads to a complex rate law, some rate constant ratios can be estimated. For example when $-\Phi\{O_3\}$ has achieved 1/2 of its increase in Fig. 7 (i. e. $-\Phi\{O_3\} = 12$), then $k_3[O_3] = k_9[H_2O]$. Thus $k_9/k_3 \simeq 1.5$. This value is more than three times larger than found by Biedenkapp et al.⁴⁸ However, when combined with our value of k_{16}/k_3 at 2537 Å, it gives $k_9/k_{16} = 3.0$ in very good agreement with the value of 2.76 found for k_9/k_{16} by Scott and Cvetanović.³⁸

Under most of our conditions reaction 20 is unimportant. In fact it is only of significance at all for the high H_2O vapor pressures in Fig. 7. With $[H_2O] = 24$ torr, $[O_3] = 1.1$ torr, and $I_a = 3\mu/\text{min.}$, then $-\Phi\{O_3\} = 16$, a reduction of about 2.5 from its maximum value. Thus for these conditions $k_{20}[H_2O] \simeq \frac{2.5}{12} k_{19} (I_a/k_{18})^{1/2}$. This leads to $k_{18}^{1/2} k_{20}/k_{19} = 9.1 \times 10^{-3} \text{ M}^{-1/2} \text{ sec}^{-1/2}$. The best value⁶¹ for k_{18} is $1.55 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. Since k_{19} cannot be more than 300 times larger (and probably no more than 10 times larger) than k_{18} , $k_{20} < 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ and probably $< 3 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$. This is a small rate constant for vibrational energy removal, corresponding to $10^6 - 10^8$ collisions for deactivation.

The inefficiency of H_2O in deactivating HO^\pm appears to be in marked contrast to the results of Kaufman,⁴⁵ who studied the H atom - NO_2 reaction to produce HO^\pm and found that the addition of H_2O vapor upstream of the O_3 inlet could eliminate the reaction of HO^\pm with O_3 . He did not report his experimental conditions, so that it is not clear how efficient the reaction

was. However, for typical flow tube conditions ($[H_2O] = 1.0$ torr, flow velocity = 100 cm/sec, displacement between H_2O and O_3 inlets = 100 cm) the number of collisions with H_2O would be $\sim 10^7$ before reaching the O_3 inlet.

A more detailed comparison can be made with the observation of Biedenkapp et al.⁴⁸ They found that $HO(v = 1)$ was not quenched by 0.05 torr H_2O vapor in 20 μ sec (100 collisions), but that it was quenched in 150 μ sec (700 collisions). If $HO(v = 2)$ behaves similarly to $HO(v = 1)$, then there is a discrepancy between the two sets of data. Of course it is possible that because of anharmonicity, the match in vibrational levels between HO and H_2O is poorer with $v = 2$ or 3 than with $v = 1$, and that the efficiency of deactivating these levels is less than for $v = 1$.

If reaction 20 is ignored, eqn. II simplifies to

$$-\Phi_c \{O_3\} = 2(k_{9b}/k_9)(k_{12}/k_{19}) k_{18}^{1/2} [O_3] (\beta/I_a)^{1/2} \quad V$$

where

$$-\Phi_c \{O_3\} \equiv -\Phi \{O_3\} - 3 - \alpha - \frac{(2k_{3a} + k_{3b}) [O_3]}{k_3 [O_3] + k_9 [H_2O]} \quad VI$$

With the values of $k_{3a}/k_3 = 0.75$ and $k_9/k_3 = 1.5$, $\Phi_c \{O_3\}$ and β can be computed. This has been done for the appropriate data in Table V, and a log-log plot is shown in Fig. 8.

The data points in Fig. 8 are badly scattered, but a straight line of slope one is drawn to fit the data. Its intercept of 0.72 torr^{-1/2}

$\text{min}^{-1/2}$ is the value of $(k_{9b}/k_9) (k_{12}/k_{19}) k_{18}^{1/2}$. This corresponds to a value of $12.7 \text{ M}^{-1/2} \text{ sec}^{-1/2}$. Since the best value⁶¹ for k_{18} is $1.55 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, and k_{12} is almost surely smaller than k_{19} , then $k_{9b}/k_9 > 3 \times 10^{-4}$.

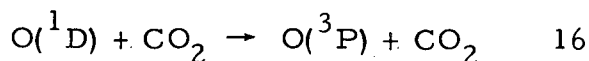
In spite of the scatter of the data in Fig. 8, there are some trends which are apparent. The data points at 2800 Å generally lie below those at the lower wavelengths. This suggests that the translational energy in the $\text{O}(^1\text{D})$ atom may affect the value of k_{9b}/k_9 ; the more energy, the higher the value. In fact one would expect this to be the case.

It is also clear from the data that the points for values of $[\text{H}_2\text{O}]/(\beta I_a)^{1/2} > 100 \text{ torr}^{1/2} \text{ min}^{-1/2}$ lie lower than those for $[\text{H}_2\text{O}]/(\beta I_a)^{1/2} < 20 \text{ torr}^{1/2} \text{ min}^{-1/2}$. At the higher values of the parameter, reaction 20 is playing some role, being about 30% as important as reaction 19 as a deactivating step. Thus the ratio $k_{18}^{1/2} k_{20}/k_{19}$ is about $0.02 \text{ M}^{-1/2} \text{ sec}^{-1/2}$ in reasonable agreement with our previous estimate.

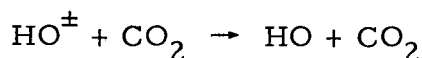
It is now apparent why in some experiments the water-chain seems to vary inversely with $I_a^{1/2}$, whereas in others it is nearly independent of I_a . For different conditions the termination may be either by radical-radical steps or by deactivation of HO^\pm by H_2O .

CO_2 Present

With CO_2 present there are two possible additional reactions. One of these is reaction 16



The other is the quenching of HO^\pm



From our results there is no evidence that the deactivating reaction is important, and we shall neglect it. Then the mechanism predicts that

$$-\Phi'\{O_3\} = 3 + \alpha' + (2k_{3a} + k_{3b})[O_3] / (k_3[O_3] + k_9[H_2O] + k_{16}[CO_2]) + \frac{2(k_{9b}/k_9) k_{12}[O_3] \beta'}{k_{19}(I_a \beta' / k_{18})^{1/2} + k_{20}[H_2O]} \quad \text{VII}$$

where

$$\alpha' \equiv (k_{3a}[O_3] + k_9[H_2O] + k_{16}[CO_2]) / (k_3[O_3] + k_9[H_2O] + k_{16}[CO_2]) \quad \text{VIII}$$

and

$$\beta' \equiv k_9[H_2O] / (k_2[O_3] + k_9[H_2O] + k_{16}[CO_2]) \quad \text{IX}$$

If reaction 20 is ignored, a comparison of the rate expression in the absence and presence of CO_2 leads to the simple result

$$(\Phi_c\{O_3\} / \Phi_c'\{O_3\})^2 = 1 + \frac{k_{16}[CO_2]}{k_9([H_2O] + k_3[O_3]/k_9)} \quad \text{X}$$

where

$$-\Phi_c'\{O_3\} \equiv -\Phi'\{O_3\} - 3 - \alpha' - \frac{(2k_{3a} + k_{3b})[O_3]}{(k_3[O_3] + k_9[H_2O] + k_{16}[CO_2])}$$

Both $-\Phi_c\{O_3\}$ and $-\Phi_c'\{O_3\}$ can be computed using $k_{3a}/k_3 = 0.75$, $k_3/k_9 = 0.67$ and $k_{16}/k_9 = 0.33$. Likewise $[CO_2]/([H_2O] + k_3[O_3]/k_9)$ can be computed. The appropriate plot is shown in Fig. 9.

The data points in Fig. 9 are extremely badly scattered. This occurs because both $\Phi_c\{O_3\}$ and $\Phi'_c\{O_3\}$ are computed as the differences between numbers which are often similar. The uncertainty is compounded when the ratio is taken, and even this ratio is squared. Nevertheless, if we force a line with an intercept of unity through the data then the slope of this line, which corresponds to k_{16}/k_9 , is about 0.3 in satisfactory agreement with the value of 0.36 found by Scott and Cvetanovic.³⁸

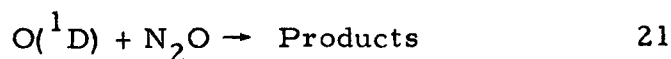
Of course the argument can be raised that values of k_{16}/k_9 and k_9/k_3 were assumed and used in computing both coordinates for Fig. 9. However, in most cases only minor corrections resulted from their use, and large errors in the values would not have influenced the outcome significantly. In any case, our results with wet ozone in the presence of CO_2 are consistent with all of our other results.

PHOTOLYSIS OF O_3 - N_2O MIXTURES

Results

When O_3 was photolyzed to 1-2% conversion in the presence of N_2O , $-\Phi\{O_3\}$ dropped, reaching about 4. The data at the three wavelengths are shown in Figs. 10 and 11. For these experiments, the quantum yields are based on absolute actinometry and not on $-\Phi_\infty\{O_3\}$ in the presence of CO_2 . The values of $-\Phi_\infty\{O_3\}$ for N_2O are listed in Table I, and they are virtually identical to those with CO_2 and N_2 .

The results at 2800 and 2288 Å are shown in Fig. 10. The half-quenching ratio is about 1.5 at 2800 and about 4.0 at 2288 Å. Though the scatter in each set of data is considerable, there is no doubt that there is a wavelength effect. The quenching can be associated with the competition between reaction 3 and reaction 21



The wavelength effect reflects the influence of excess translational energy in the $O(^1D)$ atom. At the half-quenching point $k_3[O_3] = k_{21}[N_2O]$, so that the half-quenching ratio equals k_3/k_{21} . Our results agree with those of Goldman et al.⁵² who photolyzed O_3 in the presence of N_2O at 2537 and 2288 Å and measured the N_2 yield rather than the O_3 decay. They found $k_3/k_{21} = 2.6$ at 2537 Å, which is intermediate to our two values, and $k_3/k_{21} = 4.1$ at 2288 Å in excellent agreement with our value.

At 2537 Å, we do not have good half-quenching measurements, but data were taken for various conversions and absorbed intensities. The results are shown in Fig. 11. I_a was varied from 3 to 30 μ /min., but this

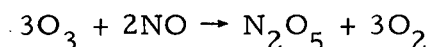
had no effect on the results. However, a noticeable effect was observed with increases in percent conversion. As the percent of O_3 converted increased, $-\Phi_{\infty}\{O_3\}$ dropped, reaching about 2.8 ± 0.6 at our most extended conversions. It is interesting to note that the $[N_2O]/[O_3]$ ratio is about 2-3 which reduces $-\Phi\{O_3\}$ half way between its values of 4.1 at low ratios and 2.8 at high ratios. This should correspond to k_3/k_{21} at 2537 Å, and the value of 2-3 is consistent with that of Goldman et al.⁵²

The drop in $-\Phi\{O_3\}$ at longer conversions might have been attributed to reaction 7 which could become important as O_2 accumulates. Actually this is not the case, as shown by two experiments at 5-15% conversion in which 0.35 torr of O_2 was added initially. This amount of O_2 is more than would have been produced by complete conversion of the 0.18 torr of O_3 . Yet the results with O_2 added are no different than with O_2 absent for the same conversion, i. e. $-\Phi\{O_3\}$ is larger than for higher conversions.

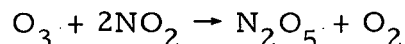
The reason why reaction 7 is unimportant in this system is because NO_2 is produced as a product. (Even though the NO_2 further reacts with O_3 to produce N_2O_5 , an equilibrium is established, and some NO_2 is present.) The rate constant for the $O(^3P) + NO_2$ reaction is $3.6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ at room temperature⁶² whereas that for reaction 7 is $2 \times 10^8 \text{ M}^{-2} \text{ sec}^{-1}$ for N_2 as a chaperone.⁶³ With N_2O as a chaperone, the rate constant is probably somewhat larger. With 20 torr N_2O the $O(^3P) + NO_2$ reaction will be more important than reaction 7 for $[NO_2]/[O_2] > 10^{-4}$. Since $[NO_2]$ almost surely reaches a value $> 10^{-4}$ torr very quickly and since $[O_2] = 0.35$ torr, reaction 7 is never significant in this system.

Another possible explanation for the low values of $-\Phi\{O_3\}$ at high conversions could be an experimental artifact due to optical absorption of

one of the products, NO_2 or N_2O_5 , both of which absorb radiation at 2537 Å. To check this possibility, mixtures of NO and O_3 were reacted. When small amounts of NO were added to excess O_3 , the optical absorption dropped immediately to a value expected from O_3 alone for the overall stoichiometric reaction



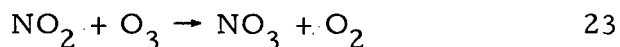
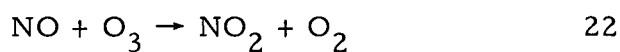
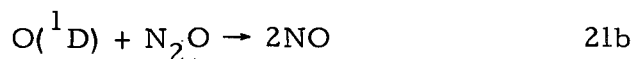
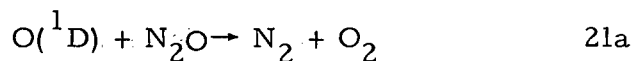
When the stoichiometric amount of NO was used, the light absorption dropped practically to zero. These experiments were repeated with 50% NO_2 diluted in O_2 replacing the NO, and identical results were obtained based on the stoichiometric relation

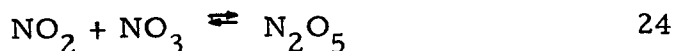


The O_3 removal rate was consistent with the known rate constant, ⁶⁴ (reaction complete in <6 sec). It is clear that the extinction coefficients of both NO_2 and N_2O_5 are sufficiently smaller than that of O_3 , so that these molecules do not interfere with the optical analysis for O_3 decay.

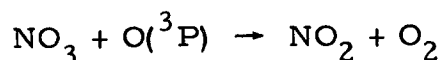
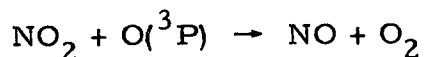
Mechanism

In addition to the steps in the pure O_3 system, reactions 1a and 2-5, the following reactions are important in the presence of N_2O

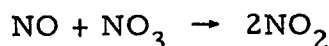




There are other reactions that also occur. For example the $\text{O}(^3\text{P})$ atom may be removed by NO_2 or NO_3 rather than O_3



However, these reactions are immediately followed by the rapid reactions 22 and 23, respectively, so that kinetically they are indistinguishable from reaction 4. Also NO may react with NO_3 .



Again this reaction followed by reaction 23 is kinetically indistinguishable from reaction 22 followed by reaction 23, and can also be ignored (or included).

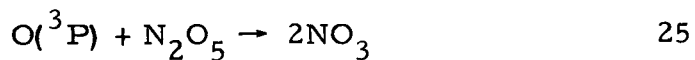
Other reactions that can be envisioned are unimportant. Deactivation of $\text{O}_2(^1\Delta)$ by N_2O is much too slow to play any role.⁶⁵ The reaction of 2NO_3 molecules is also too slow ($k = 3.7 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$)⁶⁶ to compete with the rapid reaction of NO with NO_3 ($k = 3-6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$).⁶⁶

The rate constant ratio k_{21a}/k_{21} has been shown to be ~ 0.37 , at least at 2537 and 2288 Å,⁵³ though a value as high as 0.50 is possible.⁶⁷ Under ordinary conditions, the equilibrium in reaction 24 is shifted far to the right, K_{24} , $_{-24}$ being $0.8 \times 10^{10} \text{ M}^{-1}$ at 25°C.⁶⁶ If this situation prevails, then in excess N_2O , the mechanism predicts that $-\Phi_{\infty}\{\text{O}_3\} = 4.9$ for $k_{21a}/k_{21} = 0.37$. If k_{21a}/k_{21} is as large as 0.50, then $-\Phi_{\infty}\{\text{O}_3\}$ should be 4.5.

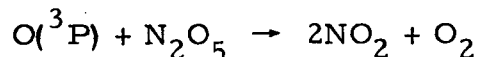
In our system, however, NO is continually being produced and it reacts readily with NO_3 ($k = 3 - 6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$) at 298°K .⁶⁶ Consequently the equilibrium in reaction 24 may be shifted to the left. Computations based on our reaction conditions and the known rate constants indicate that the shift is negligible.

The situation is that $-\Phi_\infty\{\text{O}_3\}$ should be at least 4.5 and probably 4.9. Under none of our conditions with excess N_2O was such a large value observed. The only explanation is that one of the products must be scavenging $\text{O}_2(^1\Delta)$ or $\text{O}(^3\text{P})$ in such a way that $-\Phi\{\text{O}_3\}$ is reduced. This reaction must be efficient, and proceed to a measureable extent even at 1-2 % conversion.

The most obvious possibility of a scavenger is N_2O_5 , since it and O_2 are the only major products, and O_2 has been shown to be inefficient in this system. To test this possibility, we did the following pair of experiments. In one experiment, NO_2 was reacted with 0.20 torr of O_3 , so that 15% of the O_3 was consumed. Three torr of CO_2 was added which then made a mixture consisting of 3 torr CO_2 , 0.17 torr O_3 , 0.3 torr N_2O_5 and 0.3 torr O_2 . The mixture was then photolyzed and the rate of O_3 disappearance measured. In the other experiment of the pair, pure O_3 was photolyzed to 15% conversion, 3 torr of CO_2 added, and then the mixture photolyzed. In both photolyses the reaction mixtures contained 3 torr of CO_2 and 0.17 torr of O_3 . However, the former mixture also contained 0.3 torr each of N_2O_5 and O_2 , whereas the latter contained 0.45 torr of O_2 only. This pair of experiments was repeated three times, and in each case the rate of O_3 disappearance was always 30% lower in the former mixture, in spite of the fact that there was more O_2 in the latter mixture. It is clear that N_2O_5 deactivates either $\text{O}(^3\text{P})$ or $\text{O}_2(^1\Delta)$, or both. In the case of $\text{O}(^3\text{P})$ the reaction would have to be

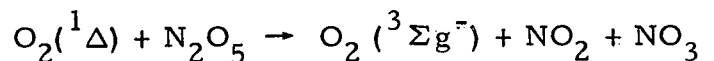


rather than



in order to cause a reduction. Both reaction 25 and deactivation of $\text{O}_2(^1\Delta)$ by N_2O_5 lead to the result that in excess N_2O , $-\Phi_\infty\{\text{O}_3\}$ should drop to 2.5-2.9 at very large conversions in accordance with our findings at 2537 Å. The relative rate constant for the competition between O_3 and N_2O_5 for either $\text{O}(^3\text{P})$ or $\text{O}_2(^1\Delta)$, as the case may be, can be estimated to be ~ 0.8 , the reaction with N_2O_5 being slower.

The possibility of deactivation of $\text{O}_2(^1\Delta)$ by N_2O_5 via the dissociative reaction



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is particularly intriguing since the reaction is 2 kcal/mole exothermic.

ACKNOWLEDGMENT

Discussions with Drs. R. Simonaitis and M. Nicolet were extremely beneficial and we are pleased to acknowledge our thanks to them. Correspondence with Professor R. Wayne was most helpful, and we appreciate his interest in our work. This work was supported by the Atmospheric Sciences Section of the National Science Foundation under Grant No. GA 12385 and by the National Aeronautics and Space Administration under Grant No. NGL-009-003 for which we are grateful.

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TABLE I

Limiting Values for the Ozone Photodecomposition Quantum Yields

λ , A	[O ₃], Torr	I _a , μ /min.	$-\Phi_o\{O_3\}$	$-\Phi_{\infty}\{O_3\}$ for M =		
				CO ₂	N ₂	N ₂ O
2800	1.0	7.0	5.8 ± 0.3	4.25 ± 0.4	-	4.15 ± 0.5
2537	0.24	3.0	5.0 ± 0.3	4.1 ± 0.4	3.85 ± 0.4	3.9 ± 0.3
2288	0.85	2.0	5.9 ± 0.3	4.4 ± 0.4	-	4.4 ± 0.5

TABLE II

Effect of Absorbed Intensity in the Photolysis of Dry O_3
at 0.14 torr and 2537 Å

$I_a, \mu/\text{min}$	$-\Phi \{O_3\}$
0.15	5.2
0.25	5.6
2.0	5.6
50	4.9
65	5.3

TABLE III
Relative Quenching Constants for $O(^1D)$

Ratio	Irradiation Wavelength, Å		
	2288	2537	2800
k_{16}/k_3	0.4 ± 0.1	0.4 ± 0.1	0.5 ± 0.1
k_{17}/k_3	0.08 ± 0.02	0.11 ± 0.02	0.08 ± 0.02
k_9/k_3	-	-	1.5^a
k_{21}/k_3	0.25	~ 0.4	0.67

a) From Figure 7

TABLE IV
Value of k_{17}/k_{16}

Source of $O(^1D)$	λ , Å	Excess Energy, kcal/mole ^a	k_{17}/k_{16}	Reference
$O_2 + h\nu \rightarrow O(^1D) + O(^3P)$	1470	0 ^b	0.35	Lowenstein ⁵⁵
$NO_2 + h\nu \rightarrow NO + O(^1D)$	2288	5.2	0.24	Preston and Cvetanović ⁵⁶
$O_2 + h\nu \rightarrow O(^1D) + O(^3P)$	1470	<15 ^c	0.21, 0.26	Young et al. ¹⁰
$O_2 + h\nu \rightarrow O(^1D) + O(^3P)$	1470	15	0.067	Warneck and Sullivan ⁵⁷
$O_2 + h\nu \rightarrow O(^1D) + O(^3P)$	1470	15	30	Noxon ²⁹
$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$	2880	21	0.17	This work
$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$	2537	28	0.28	This work
$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$	2537	28	0.23	DeMore ⁵⁸
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	2139	31	0.31	Paraskevopoulos and Cvetanović ¹²
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	2139	31	0.29	Yamazaki ⁵⁹
$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$	2288	37	0.21	This work
$N_2O + h\nu \rightarrow N_2 + O(^1D)$	1849	45	0.26	Yamazaki and Cvetanović ^{37, 60}

a) Maximum possible translational energy in $O(^1D)$.

b) Excess He added as a buffer gas.

c) Ar added to partially buffer gas mixture.

TABLE V

Photolysis of Wet Ozone

$[H_2O]$, Torr	I_a , $\mu/min.$	$-\Phi\{O_3\}$	$[CO_2]$, Torr	$-\Phi'\{O_3\}$
$\lambda = 2800 \text{ A}, [O_3] = 0.20 \text{ torr}$				
0.195	0.90	7.2		
11.6	0.90	5.7		
$\lambda = 2800 \text{ A}, [O_3] = 0.60 \text{ torr}$				
0	2.2	5.7		
0.25	2.2	10.5		
0.6	2.2	15		
5.2	2.2	14		
20	2.2	10.5		
$\lambda = 2800 \text{ A}, [O_3] = 1.1 \text{ torr}$				
0.0	3.0	5.4		
0.006	3.0	5.4		
0.008	3.0	5.7		
0.013	3.0	7.2		
0.026	3.0	7.7	105 ^a	8.3
0.116	3.0	8.9	60 ^a	11.7
0.12	3.0	-	90 ^a	11.2
0.13	3.0	10		
0.3	3.0	11.6	24	6.5
0.7	3.0	18		
0.97	3.0	16.7		
2.5	3.0	18.5		
3.0	3.0	16.5		

TABLE V (cont.)

$[\text{H}_2\text{O}]$, Torr	I_a , $\mu/\text{min.}$	$-\Phi\{\text{O}_3\}$	$[\text{CO}_2]$, Torr	$-\Phi'\{\text{O}_3\}$
3.8	3.0	16.6	25	11.6
8.0	3.0	15		
22	3.0	16		
23	3.0	14.3		
24	3.0	15		

$\lambda = 2800 \text{ \AA}, [\text{O}_3] = 1.3 \text{ torr}$

0.010	3.4	6.6		
0.019	3.4	8.8	20	4.0
0.067	3.4	10.8		
7.1	3.4	13.8		
8.2	3.4	13.2		
20	3.4	14.1		
22	3.4	13.2		

$\lambda = 2800 \text{ \AA}, [\text{O}_3] = 1.7 \text{ torr}$

0.0	3.7	5.6		
0.05	3.7	8.2	20	5.0
0.28	3.7	14.5		
1.05	3.7	15.0	26	9.5
2.3	3.7	19	26	11
3.4	3.7	18.4		
5.3	3.7	13.8	24	11.9
21.3	3.7	18.4		
21.5	3.7	18		

TABLE V (cont.)

$[\text{H}_2\text{O}]$, Torr	I_a , $\mu/\text{min.}$	$-\Phi\{\text{O}_3\}$	$[\text{CO}_2]$, Torr	$-\Phi'\{\text{O}_3\}$
$\lambda = 2800 \text{ \AA}, [\text{O}_3] = 6.0 \text{ torr}$				
0.52	4.0	16.5	22	6.5
$\lambda = 2537 \text{ \AA}, [\text{O}_3] = 0.18 \text{ torr}$				
0.0	13	5.4		
0.0	13	5.5		
< 0.1	13	5.5		
0.39	53	4.9		
0.39	25	4.8		
0.39	4.2	6.85		
0.39	0.87	9.7		
0.43	13	5.3		
0.67	13	5.5		
0.95	13	5.7	8.5	5.1
1.06	13	-	25 ^a	5.5
1.07	13	5.7	12	5.5
1.7	13	5.7		
1.8	13	5.3		
2.0	13	5.5	15	5.15
2.4	13	5.5	14.5	4.9
3.5	13	5.3		
7.7	13	5.1		
8.5	13	5.7		
9.3	13	5.5		

TABLE V (cont.)

$[\text{H}_2\text{O}]$, Torr	$\frac{I_a}{\mu/\text{min.}}$	$-\Phi\{\text{O}_3\}$	$[\text{CO}_2]$, Torr	$-\Phi'\{\text{O}_3\}$
12.4	13	5.1		
16.4	13	5.2		
16.4	13	5.2		

$\lambda = 2288 \text{ \AA}, [\text{O}_3] = 1.1 \text{ torr}$

0.90	4.4	14.4
2.2	3.6	14.4
2.7	3.6	13.6
4.9	0.8	14.5
20	0.8	15.0

a) He rather than CO_2 added.

TABLE VI
Some Rate Constant Ratios

Ratio	Value	Units	Source
k_{3a}/k_{3b}	3.0	None	-
$k_{18}^{1/2} k_{20}/k_{19}$	0.02	$\underline{M}^{-1/2} \text{sec}^{-1/2}$	Figure 8
$\frac{k_{9a}/k_{12} k_{18}^{1/2}}{k_9 k_{19}}$	12.7	$\underline{M}^{-1/2} \text{sec}^{-1/2}$	Eqn. V, Figure 8

LIST OF FIGURES

- Fig. 1 Plot of the quantum yield of O_3 consumption vs. either $[CO_2]/[O_3]$ or $[N_2]/[O_3]$ in the photolysis of $O_3 - CO_2$ or $O_3 - N_2$ mixtures for short conversions at 2800 Å, 25°C, $[O_3] \sim 1.0$ torr and $I_a = 7.0 \mu/\text{min}$.
- Fig. 2 Plot of the quantum yield of O_3 consumption vs. $[CO_2]/[O_3]$ in the photolysis of $O_3 - CO_2$ mixtures for short conversions at 2537 Å, 25°C, $[O_3] = 0.24$ torr and $I_a = 3.0 \mu/\text{min}$.
- Fig. 3 Plot of the quantum yield of O_3 consumption vs. $[N_2]/[O_3]$ in the photolysis of $O_3 - N_2$ mixtures for short conversions at 2537 Å, 25°C, $[O_3] \sim 0.24$ torr and $I_a = 3.0 \mu/\text{min}$.
- Fig. 4 Plot of the quantum yield of O_3 consumption vs. either $[CO_2]/[O_3]$ or $[N_2]/[O_3]$ in the photolysis of $O_3 - CO_2$ or $O_3 - N_2$ mixtures for short conversions at 2288 Å, 25°C, $[O_3] \sim 0.85$ torr and $I_a = 2.0 \mu/\text{min}$.
- Fig. 5 Plot of the quantum yield of O_3 consumption vs. $[O_2][M]/[O_3]$ in the work of Heidt and Forbes.³
- Fig. 6 Semilog plot of the quantum yield of O_3 consumption vs. O_3 pressure in the photolysis of ozone at 25°C and 2800 Å:
- 2800 Å, after baking and conditioning cell
 - 2537 Å
 - ◐ 2537 Å, 13 torr He present
 - ◑ 2800 Å
 - ◒ 2850 Å

- 2800 Å, traces of H₂O present
- 2800 Å, 5 μ H₂O present
- △ 2288 Å
- ▲ 2400 Å
- ◊ from Webster and Bair³⁶
- ◈ from Webster and Bair,³⁶ large excess of He present

- Fig. 7 Plot of the quantum yield of ozone consumption vs. [H₂O]^{1/2} in the photolysis of wet ozone for short conversions at 2800 Å, 25°C, [O₃] = 1.1 torr and I_a = 3 μ /min. Open circles are for runs with 60-105 torr of He also present.
- Fig. 8 Log-log plot of the water-chain component of the quantum yield of ozone consumption vs. [O₃](β /I_a)^{1/2} in the photolysis of wet ozone at 25°C.
- Fig. 9 Plot of (Φ_c {O₃}/ Φ_c' {O₃})² vs. [CO₂]/([H₂O] + 0.67 [O₃]) in the photolysis of wet ozone in the presence of CO₂ at 25°C.
- Fig. 10 Plot of the quantum yield of O₃ consumption vs. [N₂O]/[O₃] in the photolysis of O₃ - N₂O mixtures for 1-2% conversions at 25°C and [O₃] ~ 0.9 torr. Note break in abscissa and change of scale at [N₂O]/[O₃] = 27.
- Fig. 11 Semilog plot of the quantum yield of O₃ consumption vs. [N₂O]/[O₃] in the photolysis of O₃ - N₂O mixtures for various conversions at 2537 Å, 25°C, [O₃] = 0.18 torr and I_a = 3-30 μ /min.

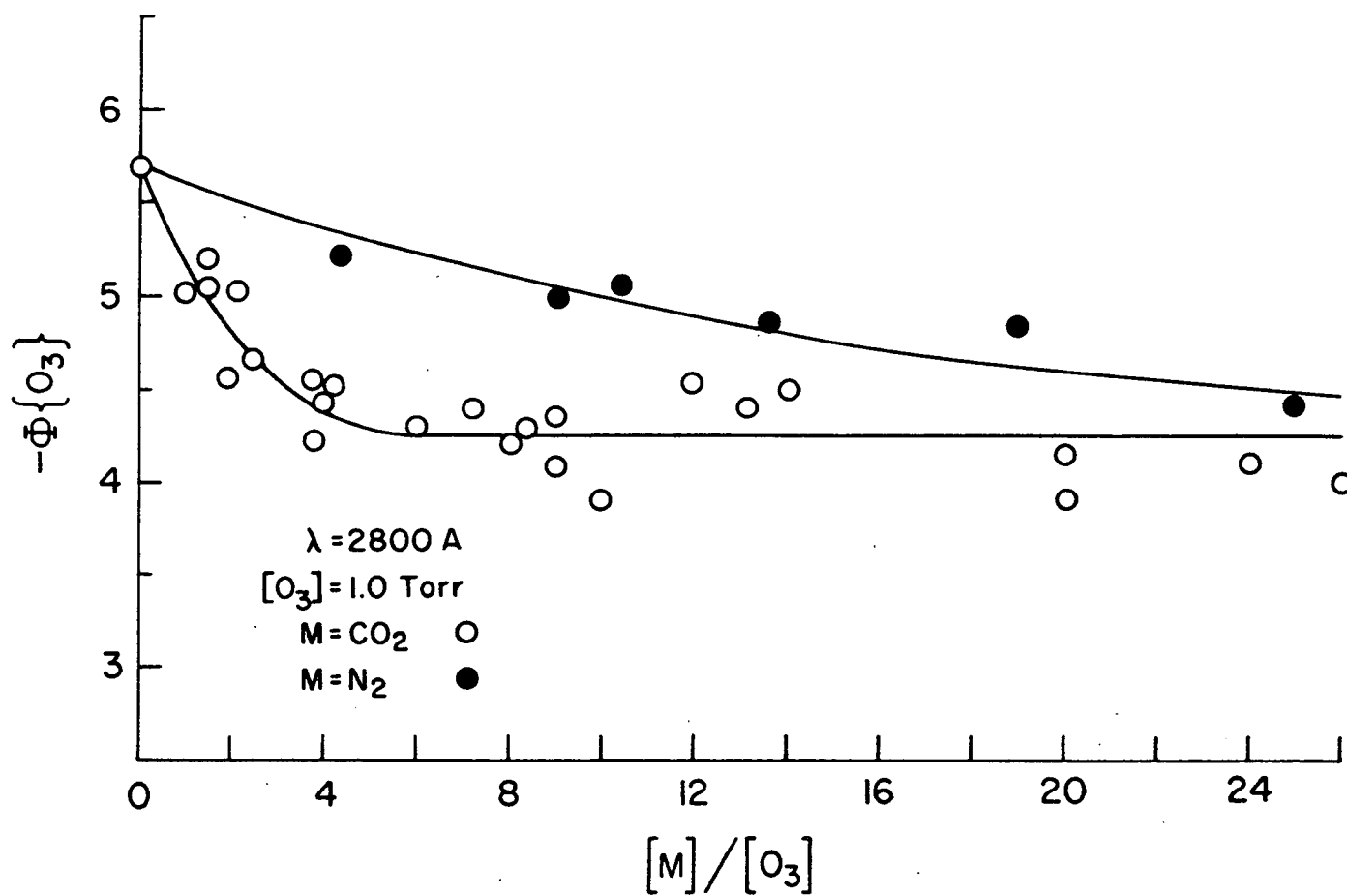


FIGURE 1

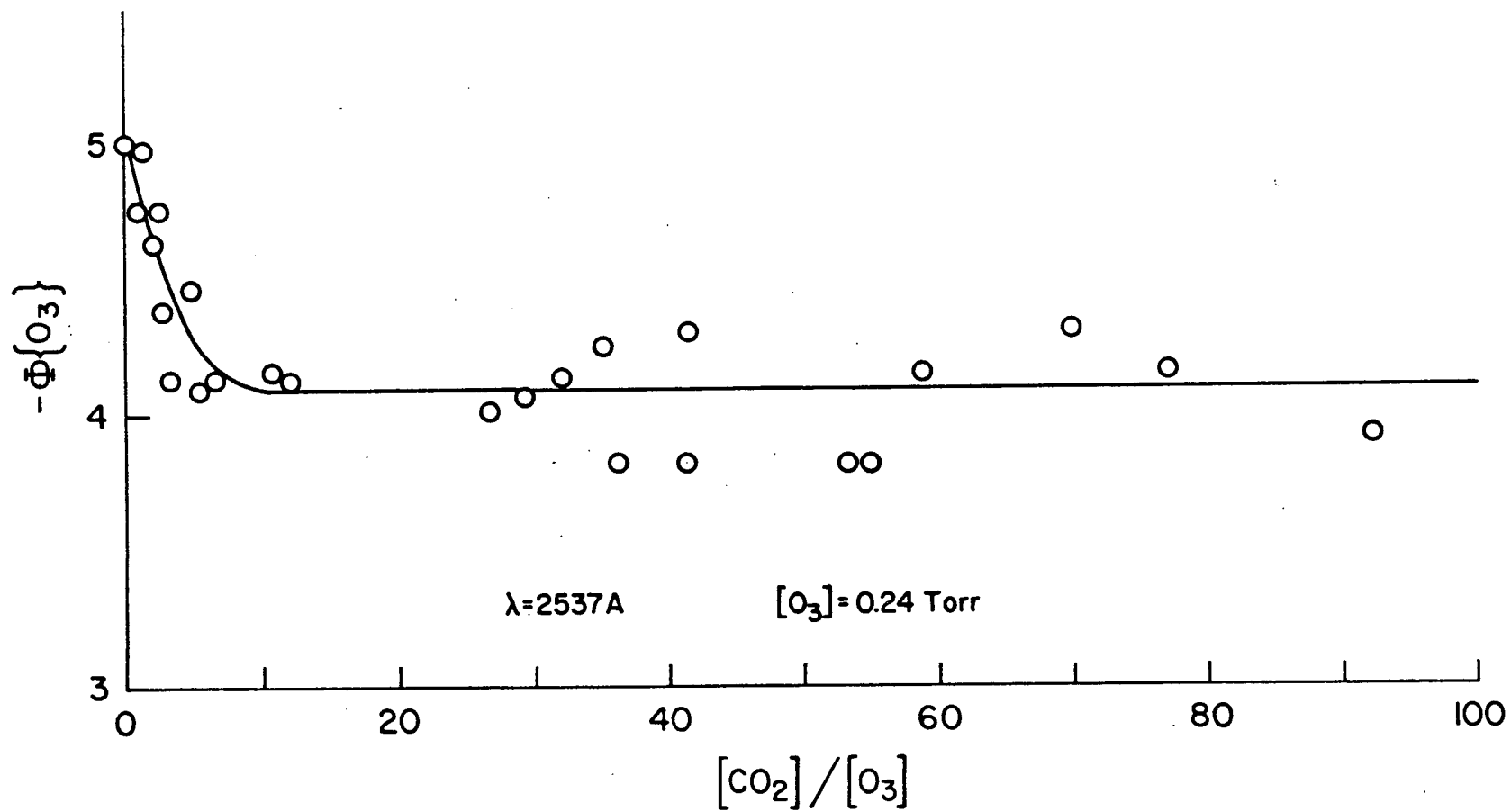


FIGURE 2

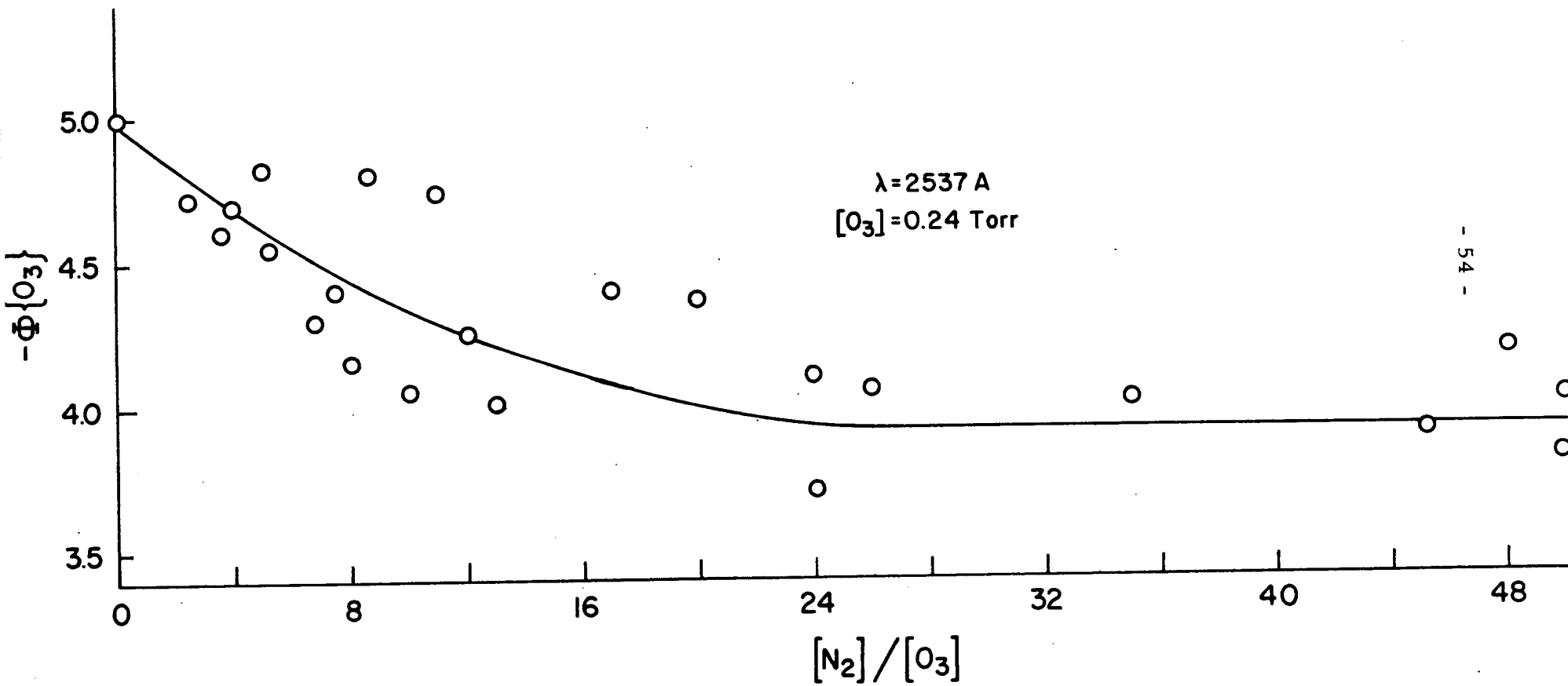


FIGURE 3

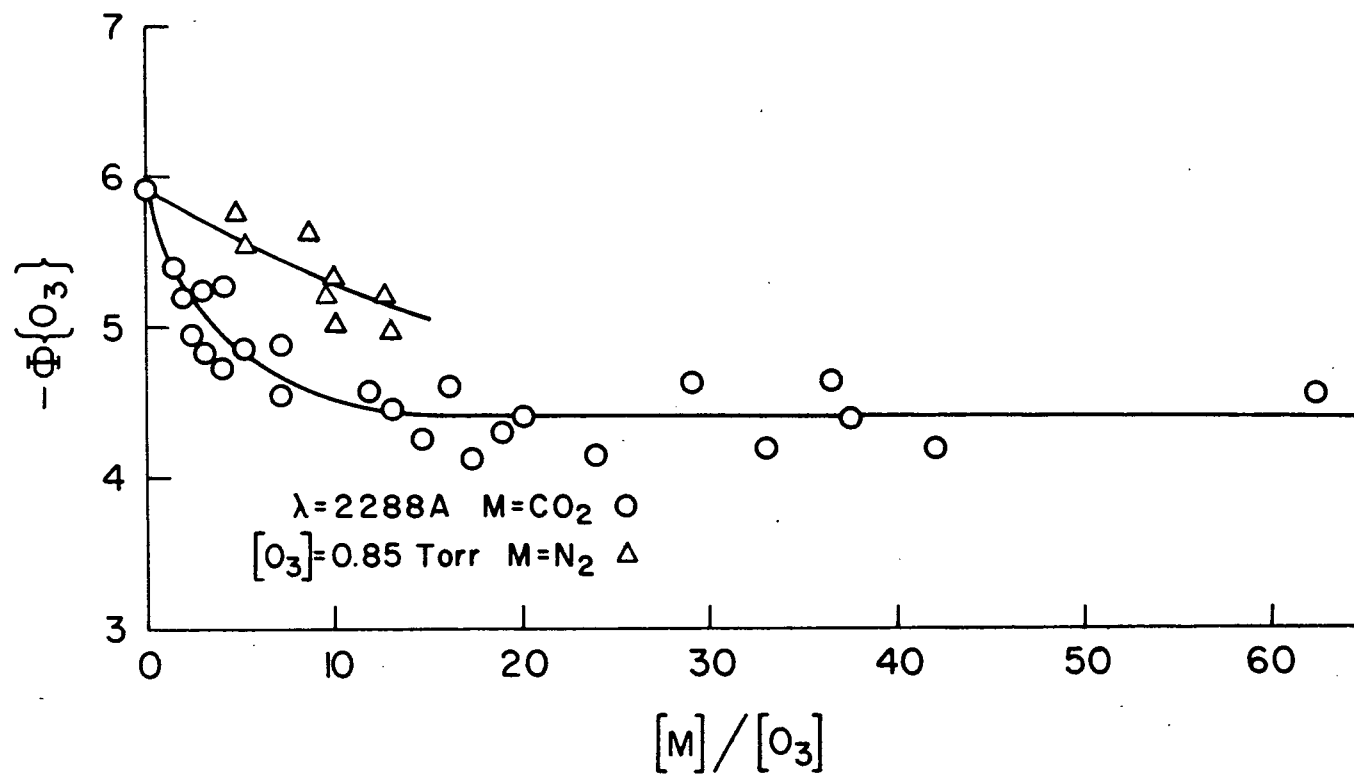


FIGURE 4

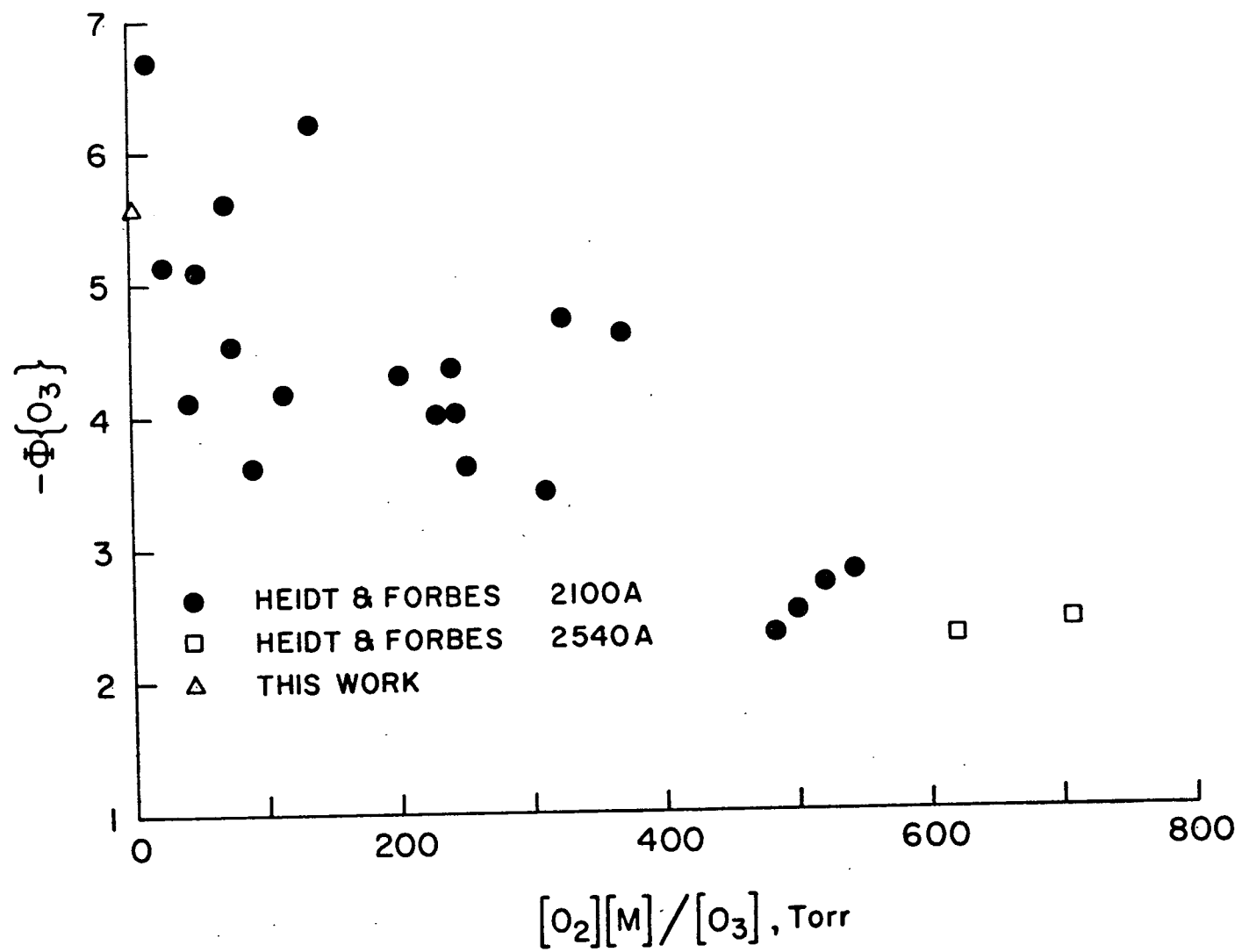


FIGURE 5

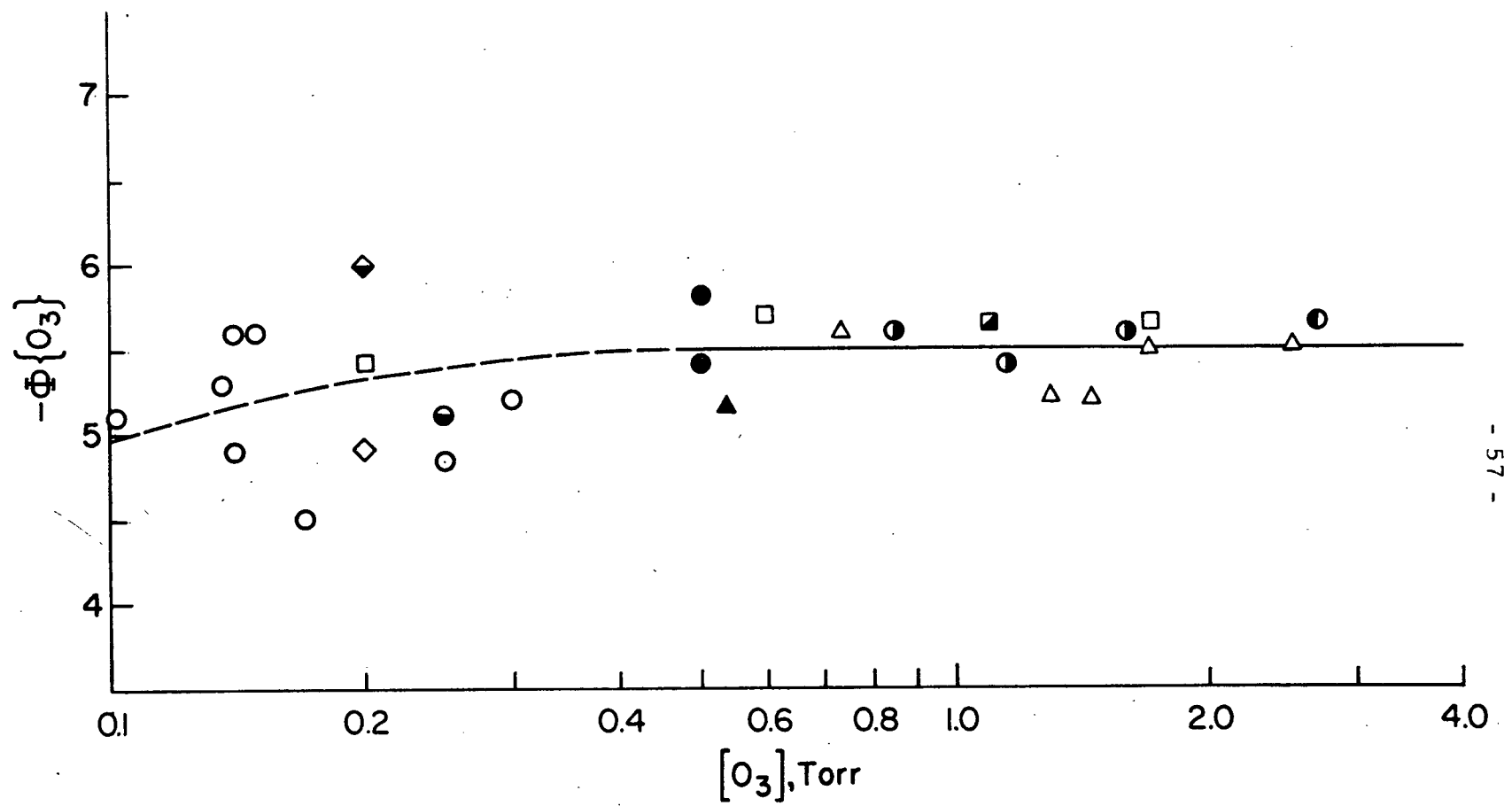


FIGURE 6

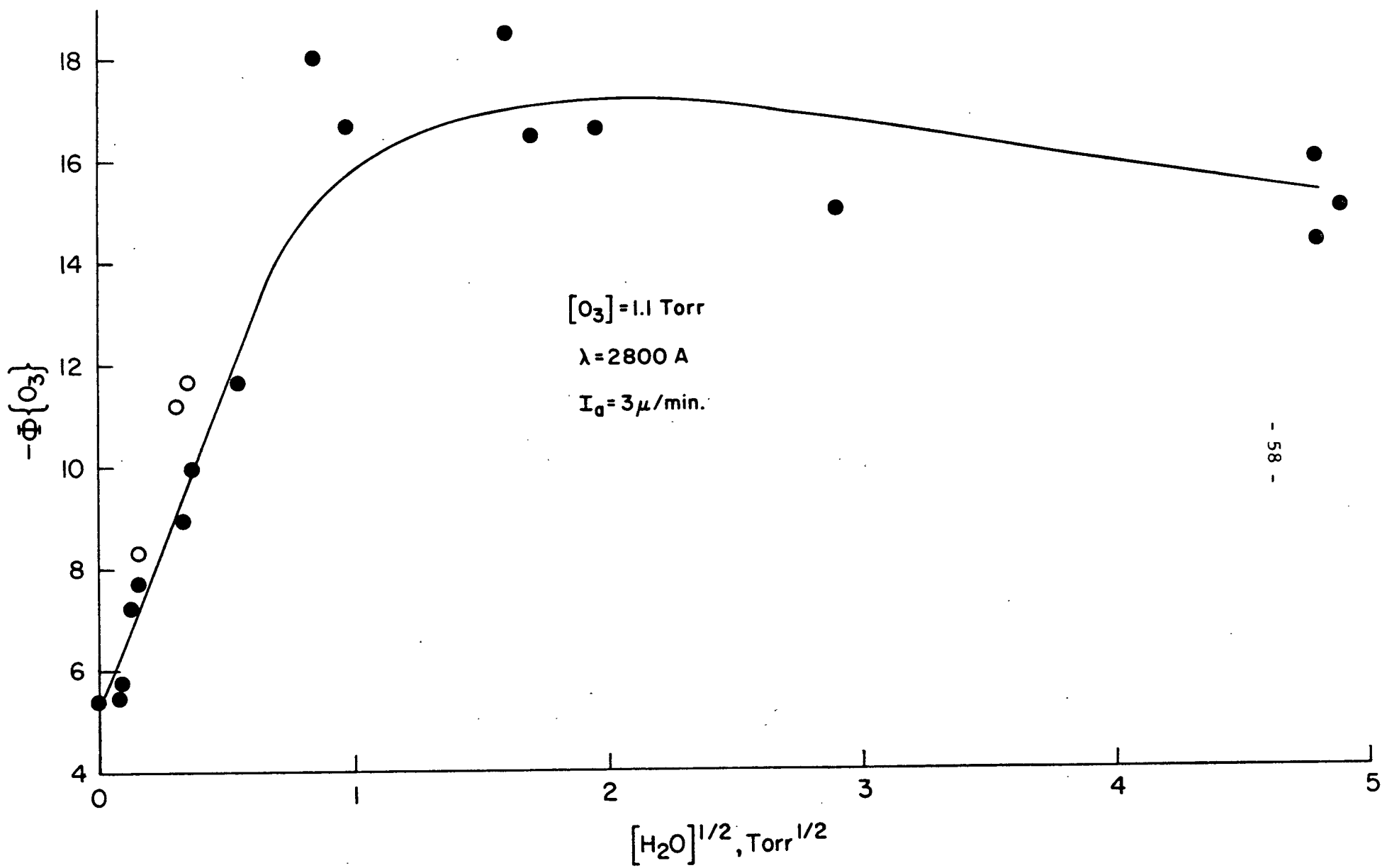


FIGURE 7

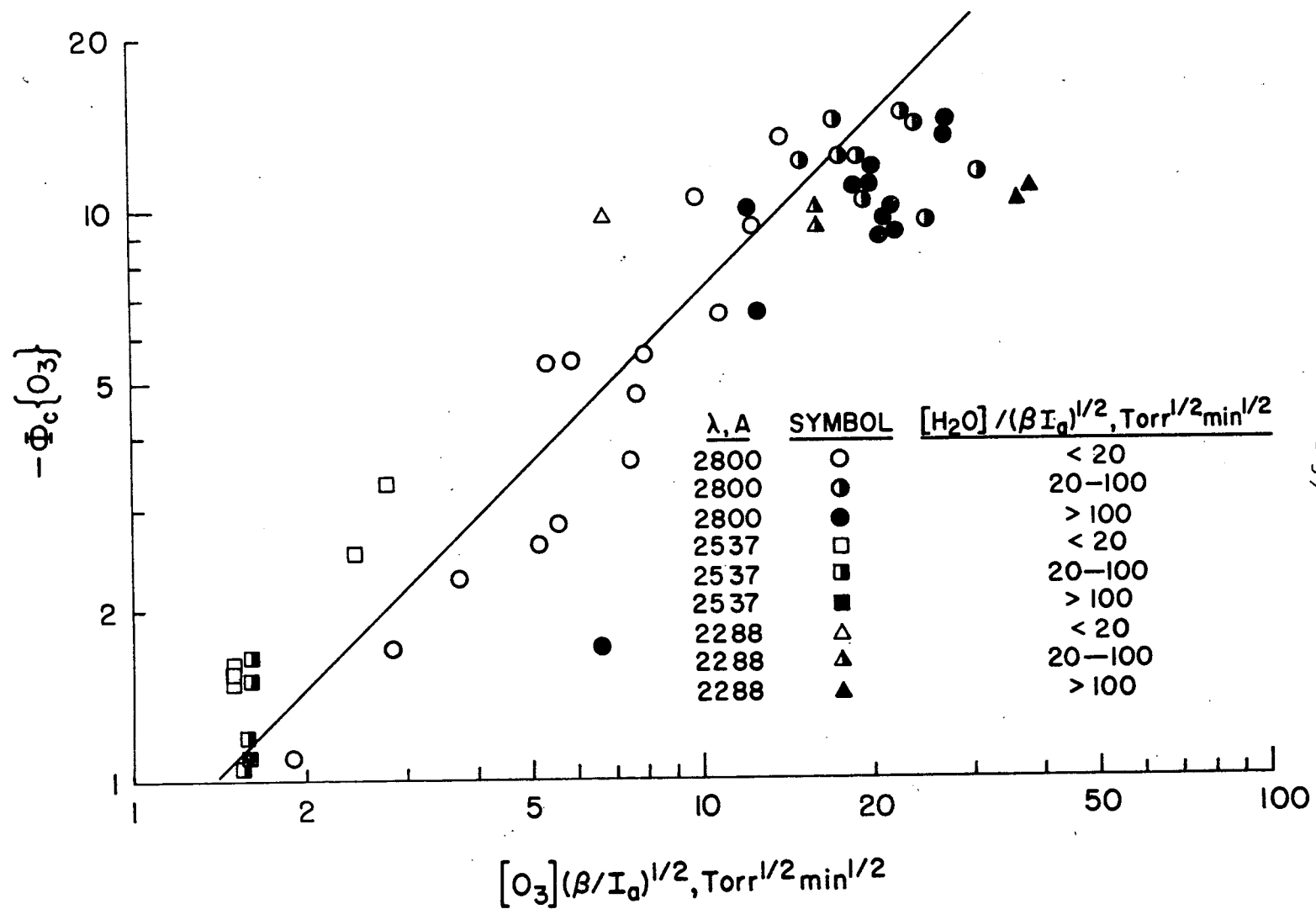


FIGURE 8

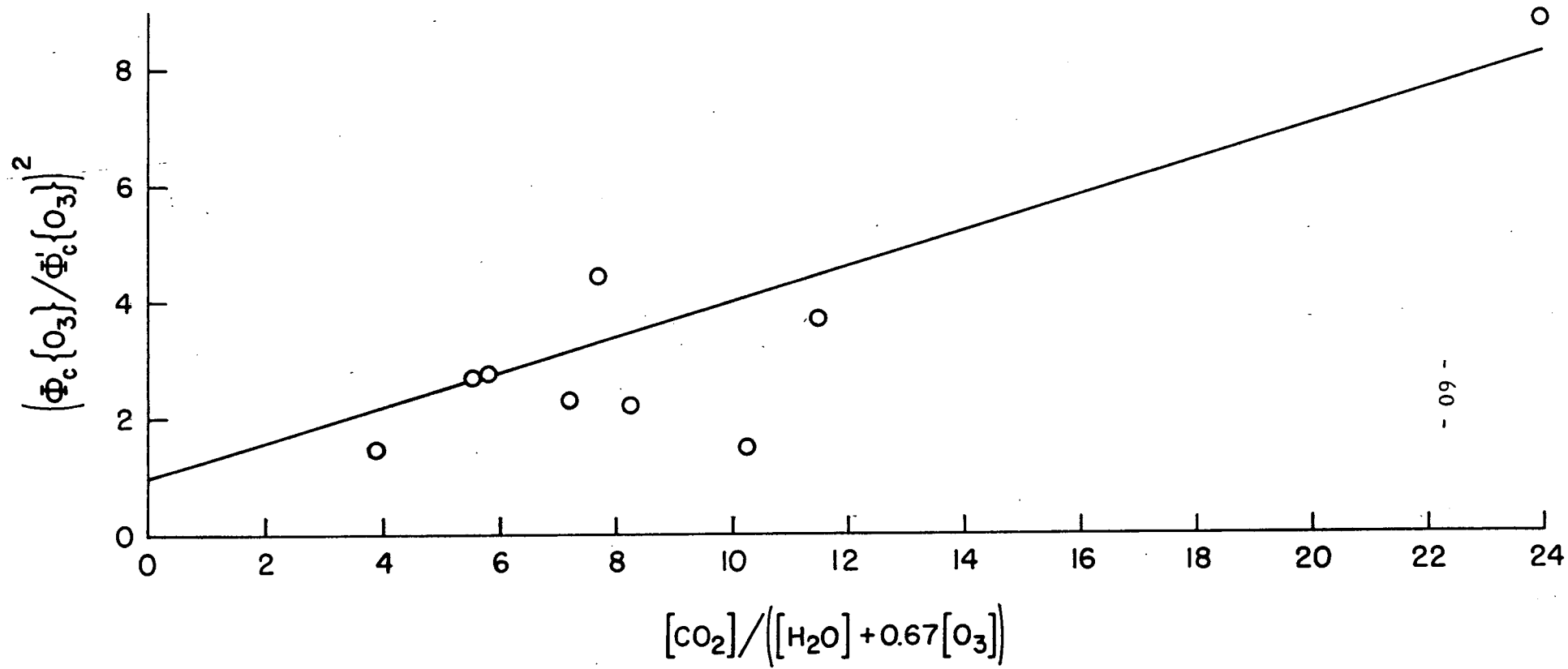


FIGURE 9

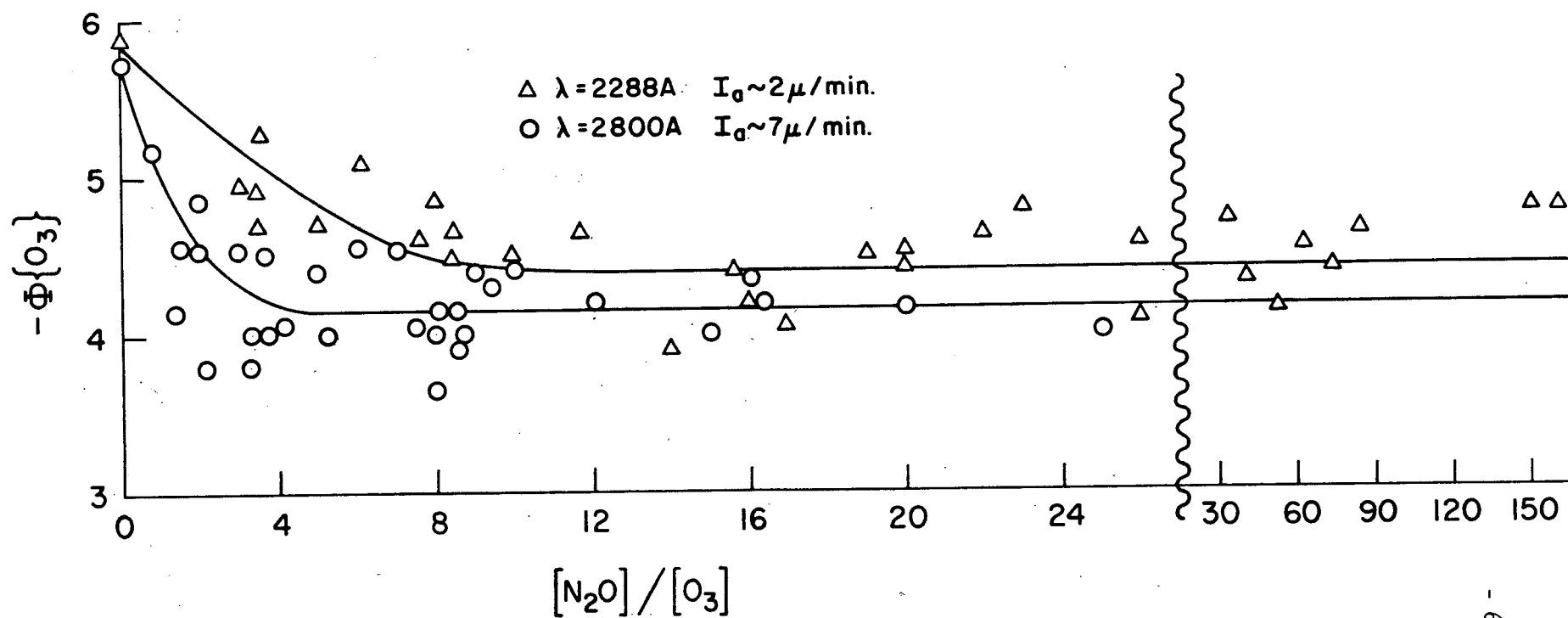


FIGURE 10

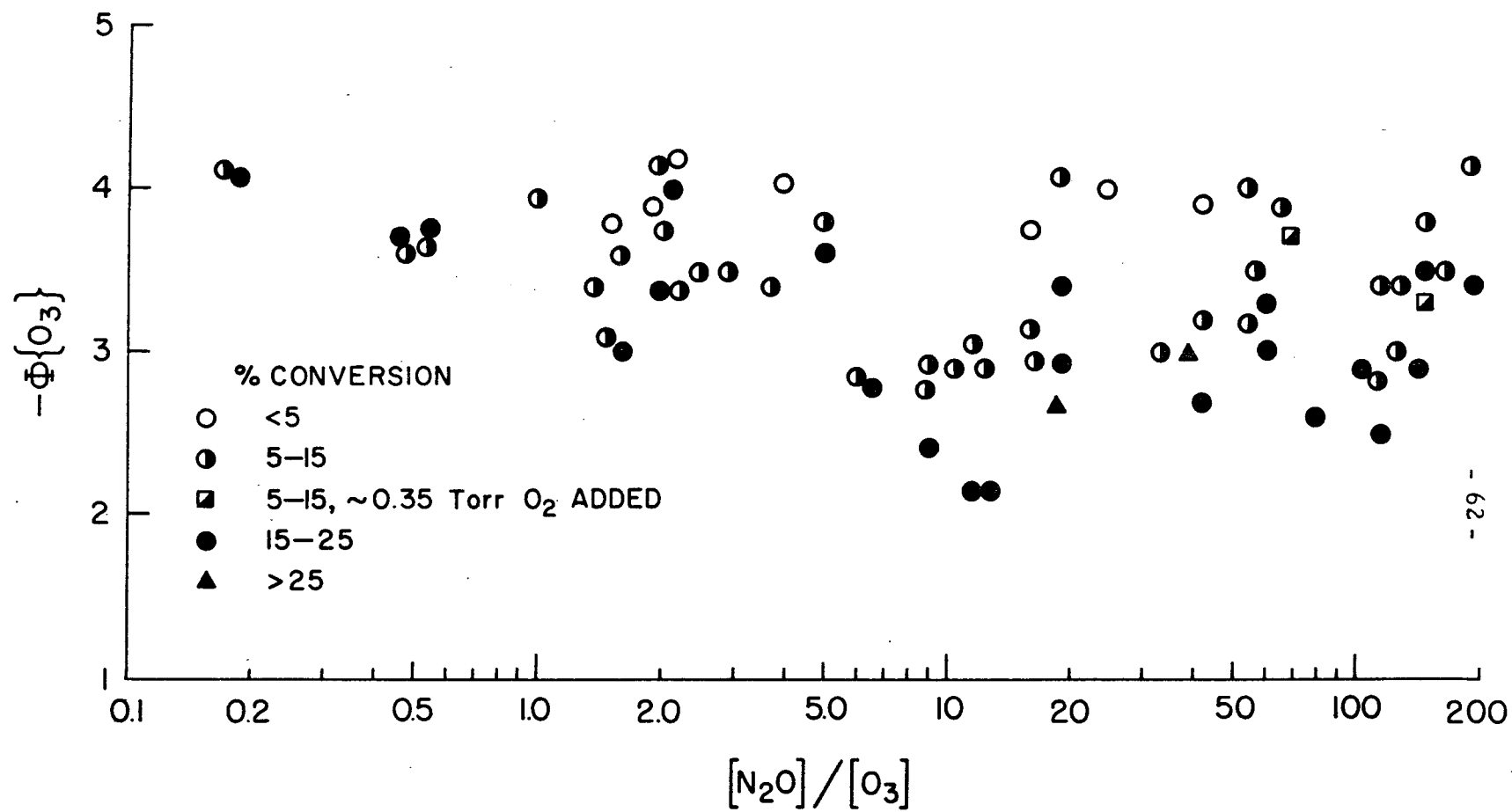


FIGURE 11